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AN ADVANCED COURSE OF
CHEMICAL CALCULATIONS

A/N. 63.

BY

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AND

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PREFACE

No apology is needed for the publication of this small book. It is. as far as we know, the first of its kind to be published in India. No doubt. there exist some good books on advanced chemical calculations written by English authors. but their prices are prohibitive, and, moreover, they do not meet the requirements of the Indian Students so weli.

The authors' teaching experience extending over several years has convinced them that until the student has attempted and solved a number of carefully selected numerical problems, he cannot get a real grasp of the basic principles of physical chemistry. The efforts of the authors at collecting suitable examples for their own students finally took the form of this book. The book covers the syllabi of B. Sc. Pass and B. Sc. Honours School Classes, and. though primarily written for their own students at the Khalsa College, will also prove useful to students of Indian Universities in general.

In the preparation of this book the authors have freely consulted standard books on Physical Chemistry and on Chemical Calculations, and express their indebtedness to all of them. They are also grateful to all their colleagues for their kind help and criticism., particularly to Professor Narain Singh, M. Sc., who has not only gone through practically the whole of the manuscript, but has also written the chapter on Electromotive Force.

KHALSA COLLEGE, AMRITSAR.
October, 1933.

NIRANJAN SINGH
JAGINDAR SINGH

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ERRATA

Before using the book please make the following corrections :—

Page	Line	For	Read.
50	13	$7{\cdot}20$	$7{\cdot}6$
51	6	$\frac{10}{342}$	$\frac{x}{60}$
62	28	100 c.c	1000 c.c.
83	15	$[N_2O]$	$[NO_2]$
85	15	Kc	Kp
87	6	$1{\cdot}1713 = \frac{1}{0{\cdot}5}$	$1{\cdot}1713 \times \frac{1}{0{\cdot}5}$
97	6	$p - 758{\cdot}01$	$p = 758{\cdot}01$
99	14	$\log\ 10 \times \frac{b(a-x)}{a(b-x)}$	$\log_{10}\frac{b(a-x)}{a(b-x)}$
109	15	mg.	gm.
110	5	$\therefore \frac{\frac{2x_2}{0{\cdot}79 - x_2}}{10}$	$\therefore \frac{\frac{2x_2}{0{\cdot}79 - x_2}}{10}$
111	13	Solven	Solvent
116	29	0·008	0·0084

AN ADVANCED COURSE OF

CHEMICAL CALCULATIONS

CHAPTER I

ORGANIC ANALYSIS

1. Estimation of Carbon and Hydrogen. Carbon and hydrogen present in an organic compound are estimated by *combustion :* A known weight of the pure dry substance is heated with dry cupric oxide in a current of oxygen. The hydrogen and the carbon present in the compound burn off to produce water and carbon dioxide. The water is absorbed in a U-tube containing anhydrous calcium chloride and the carbon dioxide in "potash bulbs" containing a strong solution of potassium hydroxide.

2. Estimation of Nitrogen. There are two different methods for the estimation of nitrogen in organic substances :—

(1) *Dumas' Combustion Method.* This is based on the fact that when a nitrogenous organic substance is combusted with cupric oxide, it gives water, carbon dioxide, and *nitrogen.* The combustion is carried out in an atmosphere of carbon dioxide, and any oxides of nitrogen formed are decomposed by passing the gases over a heated spiral of bright metallic copper. The nitrogen is collected over a strong solution of KOH (which absorbs the carbon dioxide) and measured.

(2) *Kjeldahl's Method.* On heating certain classes of organic substances with concentrated sulphuric acid and potassium sulphate, the nitrogen they contain is wholly converted into ammonia. The latter combines

with excess of the acid present to form *ammonium sulphate*. After the reaction is over, the mixture is distilled with an excess of KOH, and the liberated ammonia is estimated by absorbing it in a measured excess of a standard acid.

3. Carius' Method for the Estimation of Halogens, Sulphur, and Phosphorus. In this method the substance is heated with *fuming nitric acid* in a sealed tube. Sulphur and phosphorus are thereby oxidized to sulphuric and phosphoric acids, which are estimated by precipitation as barium sulphate and ammonium phosphomolybdate. In the estimation of a halogen the oxidation of the substance by fuming nitric acid is effected in the presence of a few crystals of *silver nitrate*. The halogen is thereby converted into the silver halide, which is separated, dried, and weighed.

4. Estimation of Oxygen. There is no direct method of estimating oxygen. The amount of this element present in an organic substance is always found by *difference*.

5. Estimation of Typical Groups :—

(1) **Carboxyl Group.** The equivalent weights of organic acids are generally determined by the analysis of their silver, calcium, or barium salts, or by direct titration against standard barium hydroxide.

(2) **Esters.** The estimation of an ester is effected by heating a known weight with an excess of alcoholic KOH :—

$$RCOOR_1 + KOH \longrightarrow RCOOK + R_1OH.$$

After the reaction is over, the unused KOH is titrated against standard HCl.

(3) **Amides.** An amide is estimated by hydrolysis with an alkali or sulphuric acid. In the former case the evolved ammonia is directly absorbed in a standard acid, and the excess of the acid titrated. In the latter case the resulting ammonium sulphate is decomposed with an excess of alkali, and the evolved ammonia is absorbed in standard acid as before.

(4) **Hydroxyl Group.** To estimate the hydroxyl group the substance is treated with acetic anhydride or acetyl chloride,

$$ROH + (CH_3CO)_2O \longrightarrow CH_3COOR + CH_3COOH$$

$$ROH + CH_3COCl \longrightarrow CH_3COOR + HCl.$$

After the reaction is complete, the mixture is treated with water to decompose the excess of the reagent, and the total acid is titrated with standard alkali.

Another method for the estimation of the hydroxyl group consists in treating the substance under examination with methyl magnesium iodide (Grignard's reagent) and measuring the volume of methane evolved.

$$ROH + CH_3MgI \longrightarrow ROMgI + CH_4.$$

(5) **Methoxyl and Ethoxyl Groups.** These are estimated by Zeisel's method, which consists in decomposing the compound with hydriodic acid :—

$$R(OCH_3)n + nHI \longrightarrow R(OH)n + nCH_3I.$$

The resulting alkyl iodide is passed into a solution of silver nitrate in 90 per cent alcohol, filtered, and weighed. An alternative method consists in decomposing the alkyl iodide by heat, absorbing the iodine thus set free in KI, and titrating against standard thiosulphate.

(6) **Mercaptans.** These may be estimated by the application of Grignard's reagent in exactly the same manner as alcohols. Another method consists in adding an excess of standard iodine solution, which removes the hydrogen attached to sulphur :—

$$2C_2H_5SH + I_2 \longrightarrow 2HI + C_2H_5S.SC_2H_5$$

Ethyl mercaptan — Ethyl disulphide

After the oxidation is complete, the iodine left over is determined by means of standard thiosulphate.

(7) **Amino and Imino Groups.** The aliphatic amines can be titrated against HCl, using methyl orange as indicator ; in the case of some aromatic amines good results are obtained with methyl red.

A most general method for the estimation of amines consists in preparing a pure sample of the platinichloride, and determining the amount of platinum it contains by igniting a known weight.

Primary and secondary amines can also be estimated by means of the Grignard reagent (compare alcohols) :—

$$RNH_2 + CH_3MgI \longrightarrow RNHMgI + CH_4$$

$$R_2NH + CH_3MgI \longrightarrow R_2NMgI + CH_4.$$

In the case of the primary amines if the temperature be raised to 120°-125°, another molecule of methane is evolved :—

$$RNHMgI + CH_3MgI \longrightarrow RN<\begin{matrix}MgI\\MgI\end{matrix} + CH_4.$$

With the secondary amines, of course, no further change is possible.

(8) **Carbonyl Group.** A known weight of the compound is mixed with an excess of a dilute solution of phenylhydrazine, and allowed to stand for 15 hours. An excess of N/10 iodine is then added. The iodine oxidizes the free phenylhydrazine to nitrogen, while the hydrazone remains unaffected.

$$C_6H_5NH.NH_2 + 2I_2 \longrightarrow 3HI + N_2 + C_6H_5I.$$

The excess of iodine is then titrated with standard thiosulphate.

Another method of estimating the carbonyl group consists in mixing N/10 solutions of the compound under investigation and of hydroxylamine in 50 per cent alcohol. When the oxime formation is complete, the excess of hydroxylamine is titrated with standard HCl, using methyl orange as indicator.

(9) **Acetyl Group.** The number of acetyl groups present in an acetyl derivative (*e.g.* that of a phenol, alcohol, or an amine) is best estimated by hydrolysing about 0·2 gm. of the substance with an excess of 10 per

cent benzene sulphonic acid solution. The mixture is distilled in a current of steam, and the distillation continued until the liquid passing over is neutral :—

$$RO.COCH_3 + C_6H_5SO_2OH \longrightarrow C_6H_5SO_2OR + CH_3COOH.$$

The whole distillate, which contains acetic acid, is titrated with standard barium hydroxide, using phenolphthalein as indicator.

An alternative method consists in heating, under a reflux condenser, 0·5 gm. of the substance with an excess of alcoholic KOH, for one hour. The liquid is acidified with phosphoric acid, and distilled in steam until the distillate is no longer acidic. The whole of the distillate is titrated with standard barium hydroxide.

(10) **Nitro, Nitroso, and Azo Groups.** These are estimated by means of standard titanous chloride solution. The nitro group requires 6 equivalents of titanous chloride for its complete reduction, while each of the nitroso and the azo groups requires 4 equivalents.

$$TiCl_3 + HCl = TiCl_4 + H$$
$$-NO_2 + 6H = -NH_2 + 2H_2O$$
$$-NO + 4H = -NH_2 + H_2O$$
$$Ar.N{:}N.Ar + 4H = 2ArNH_2.$$

A known amount of the substance is boiled for 15 minutes with a known excess of titanous chloride solution in a flask through which a stream of CO_2 passes. The excess of $TiCl_3$ is then titrated with standard ferric alum solution, using potassium sulphocyanide as an external indicator.

In the case of soluble dyes a direct titration with standard titanous chloride is carried out, the dye acting as its own indicator.

Example 1. *A substance gave the following results on analysis :*

0·1335 *gm. gave* 0·2948 *gm. of* CO_2 *and* 0·0603 *gm.* H_2O.

0·085 *gm. gave* 26·4 *c.c. of dry nitrogen measured at* 27° *and* 750 *mm.*

0·13 *gm. on vaporization in a Victor Meyer Apparatus displaced* 38·8 *c.c. of moist air at* 17° *and* 764 *mm.*

Tension of aqueous vapour at 17° = 14 *mm.*

Determine the molecular formula of the substance.

(*Punjab B. Sc.* 1930.)

Volume of dry nitrogen reduced to N.T.P.

$$= 26{\cdot}4 \times \frac{273}{273+27} \times \frac{750}{760} \text{ c.c.}$$

Weight of this volume of nitrogen

$$= 26{\cdot}4 \times \frac{273}{300} \times \frac{750}{760} \times {\cdot}00009 \times 14{\cdot}0 \text{ or } 0{\cdot}0299 \text{ gm.}$$

Percentage composion of the compound is—

$$C = 0{\cdot}2948 \times \frac{12}{44} \times \frac{100}{0{\cdot}1335} \text{ or } 60\%$$

$$H = 0{\cdot}0603 \times \frac{2}{18} \times \frac{100}{0{\cdot}1335} \text{ or } 5\%$$

$$N = 0{\cdot}0299 \times \frac{100}{0{\cdot}085} \text{ or } 35\%$$

Dividing the percentage of each element by its atomic weight, we get the *atomic ratio* :—

$$C = \frac{60}{12} = 5{\cdot}0$$

$$H = \frac{5}{1} = 5{\cdot}0$$

$$N = \frac{35}{14} = 2{\cdot}5$$

Dividing by the smallest number, 2·5, we get the *empirical formula*, C_2H_2N.

Volume of dry air, reduced to N.T.P., displaced in the Victor Meyer Apparatus

$$= 38{\cdot}8 \times \frac{273}{290} \times \frac{750}{760} \text{ or } 36{\cdot}0 \text{ c.c.}$$

Weight of this volume of hydrogen

$$= 36{\cdot}0 \times {\cdot}00009 \text{ or } 0{\cdot}00324 \text{ gm.}$$

$$\text{V.D. of the substance} = \frac{0{\cdot}13}{0{\cdot}00324} \text{ or } 40$$

Molecular Weight $= 40 \times 2$ or 80

Hence, the *molecular formula* of the substance is twice the empirical formula, *i.e.* $\mathbf{C_4H_4N_2}$.

Example 2. *A substance gave the following results on analysis :—*

0·197 *gm. gave* 0·293 *gm.* CO_2 *and* 0·150 *gm.* H_2O.

By the Kjeldahl method 0·59 *gm. required* 10 *c.c. of normal* H_2SO_4 *for neutralization of the ammonia. The original substance, when boiled with caustic soda, evolved ammonia, and the dry residue, when heated with soda lime gave off methane. What is the substance ? Explain the above reactions.*

(*Leeds Genl. Org.*, 1909 ; *Punjab B. Sc. Hons.* 1924.)

Volume of normal H_2SO_4 neutralized by ammonia

$$= 10 \text{ c.c.}$$

Hence, the weight of ammonia liberated

$$= 17 \times \frac{10}{1000} \text{ or } 0{\cdot}17 \text{ gm.}$$

Weight of nitrogen that this amount of ammonia contains $= 0{\cdot}17 \times \frac{14}{17}$ or 0·14 gm.

Percentage composition of the compound is—

$$\mathbf{C} = 0{\cdot}293 \times \frac{12}{44} \times \frac{100}{0{\cdot}197} \text{ or } 40{\cdot}6\%$$

$$\mathbf{H} = 0{\cdot}150 \times \frac{2}{18} \times \frac{100}{0{\cdot}197} \text{ or } 8{\cdot}5\%$$

$$\mathbf{N} = 0{\cdot}14 \times \frac{100}{0{\cdot}59} \text{ or } 23{\cdot}7\%$$

$$\mathbf{O} \text{ (by difference)} = 27{\cdot}2\%$$

Dividing the percentage of each element by its atomic weight, we get the *atomic ratio*—

$$C = \frac{40{\cdot}6}{12} = 3{\cdot}4$$

$$H = \frac{8{\cdot}5}{1} = 8{\cdot}5$$

$$N = \frac{23{\cdot}7}{14} = 1{\cdot}7$$

$$O = \frac{27{\cdot}2}{16} = 1{\cdot}7$$

Dividing by the smallest number, 1·7, we get the *empirical formula*, C_2H_5NO.

Since the original substance, when boiled with caustic soda, gives off ammonia, it must be an amide or the ammonium salt of a carboxylic acid. But since the molecule contains only one atom of oxygen for an atom of nitrogen, it must be an amide, and not an ammonium salt of a carboxylic acid. Hence, the constitutional formula of the substance may be written as :

$$CH_3.C\lessgtr^{O}_{NH_2}$$

That is, the substance is **acetamide**. This conclusion is supported by the evolution of methane on heating the dry residue from the first reaction with soda lime. The reactions that take place are represented below :—

(*i*) $CH_3.CO.NH_2 + NaOH \longrightarrow CH_3COONa + NH_3$
Acetamide — Sodium acetate

(*ii*) $CH_3COONa + NaOH \longrightarrow Na_2CO_3 + CH_4$
Methane

Example 3. *10 c.c. of a liquid containing urea, on treatment with an alkaline solution of sodium hypobromite, evolved 21·5 c.c. of nitrogen measured at 18°C and 740 mm. pressure. Calculate the amount of urea present in a litre of the liquid.*

Volume of nitrogen obtained from 10 c.c. of the liquid reduced to N.T.P.

$$= 21{\cdot}5 \times \frac{740}{760} \times \frac{273}{291} \text{ or } 19{\cdot}6 \text{ c.c.}$$

From the equation,

$$CO(NH_2)_2 + 3NaOBr \longrightarrow CO_2 + N_2 + 2H_2O + 3NaBr,$$

we see that 60 grams of urea, on treatment with sodium hypobromite, give 1 G.M.V. or 22·4 litres of nitrogen measured at N.T.P.

Hence, the amount of urea present in a litre of the given liquid $= 60 \times \frac{19{\cdot}6}{22400} \times \frac{1000}{10} = 5{\cdot}25$ gm.

Example 4. *A hydrocarbon of the formula* C_8H_{10} *yields, on oxidation, a colourless crystalline dibasic acid containing* 57·8 *per cent carbon and* 3·6 *per cent hydrogen. The silver salt contains* 56·8 *per cent of silver. On heating the acid, it is converted into a compound of the formula* $C_8H_4O_3$; *on distillation with lime, benzene is formed. Discuss the structure of the original hydrocarbon.*

(*Manchester B. Sc.; Punjab B. Sc.* 1921.)

The given hydrocarbon, C_8H_{10}, evidently belongs to the benzene series, the general formula for the series being C_nH_{2n-6}. This view is further supported by the fact that the acid, formed by the oxidation of the hydrocarbon, yields *benzene* on distillation with lime.

Since the hydrocarbon gives, on oxidation, a dibasic acid, there must be *two* side-chains linked to the benzene ring.

The percentage composition of the acid, formed by the oxidation of the hydrocarbon, is:

$$C = 57{\cdot}8\%$$

$$H = 3{\cdot}6\%$$

$$\therefore O = 38{\cdot}6\%$$

The simplest atomic ratio is:

$$C = \frac{57{\cdot}8}{12} \text{ or } 4{\cdot}8$$

$$H = \frac{3{\cdot}6}{1} \text{ or } 3{\cdot}6$$

$$O = \frac{38{\cdot}6}{16} \text{ or } 2{\cdot}4$$

Hence the empirical formula of the acid is $C_4H_3O_2$.

Now, the silver salt of the acid contains 56·8 per cent of silver. Hence, the equivalent weight of the silver salt

$$= \frac{100}{56{\cdot}8} \times 108 \text{ or } 190.$$

Whence, the equivalent weight of the acid

$$= 190 - 108 + 1 \text{ or } 83.$$

And, since the acid is dibasic, the molecular weight is 166. Hence, the *molecular formula* of the acid is $C_8H_6O_4$, and the constitutional formula, $C_6H_4(COOH)_2$.

Now, the acid gives, on heating, an anhydride of the formula $C_8H_4O_3$, or $C_6H_4 \langle \begin{matrix} CO \\ CO \end{matrix} \rangle O$. Hence, it must be benzene-*ortho*-dicarboxylic acid.

From the above considerations it follows:—

(*i*) That the given hydrocarbon is a homologue of benzene;

(*ii*) It contains two side chains, and

(*iii*) That the side-chains occupy ortho positions with respect to each other.

Further, since the formula of the hydrocarbon is C_8H_{10}, each of the side-chains must consist of a *methyl* group. Hence, the given hydrocarbon is ortho-dimethyl-benzene, or **ortho-xylene.**

Example 5. *A mono-acid organic base gave the following results on analysis :—*

0·100 *gm. gave* 0·288 *gm.* CO_2 *and* 0·0756 *gm. water.*

0·200 *gm. gave* 21·8 *c.c. of nitrogen at* 15°C *and* 760 *mm.*

0·400 *gm. of the platinichloride left, on ignition,* 0·125 *gm. of platinum.*

What is the molecular formula of the base ?

(*Pt* = 195.)

Note. The empirical formula of the base calculated as in the previous examples comes to C_7H_9N.

If *B* is the molecular formula of the base, the formula of the platinichloride shall be $B_2H_2PtCl_6$. A gram molecule of the platinichloride will leave on ignition 195 grams of pure platinum. Hence, the molecular weight of the platinichloride $B_2H_2PtCl_6$

$$= 0{\cdot}400 \times \frac{195}{0{\cdot}125} \text{ or } 624.$$

$\therefore$ Molecular Weight of the base *B*

$$= \frac{624 - (2 + 195 + 213)}{2} \text{ or } 107,$$

which is identical with the empirical formula weight. Hence, the molecular formula of the base is the same as its empirical formula, *i.e.* $\mathbf{C_7H_9N}$.

Example 6. 0·174 *gm. of an organic amino-acid gave on combustion* 0·392 *gm. of* CO_2 *and* 0·0795 *gm. of* H_2O. 0·30 *gm. of the substance gave* 24·57 *c.c. of* N_2 *at* 0°C. *and* 740 *mm. When diazotised and treated with KCN and hydrolysed, it gave an acid whose silver salt contained* 56·84% *Ag. This acid when heated yields an anhydride. Discuss the constitution of this acid.*

(*Punjab B. Sc.* 1931.)

The empirical formula of the acid calculated as in Example 1 comes to $C_7H_7NO_2$.

The molecular formula of the acid appears to be the same as the empirical formula. It contains seven carbon, one nitrogen, and two oxygen atoms. This shows that the acid is most probably a derivative of benzene, containing one carboxyl group and one amino group. Further, since it can be diazotized, the amino group must be linked directly to the nucleus. Hence, its formula may be assumed to be

$$C_6H_4\begin{cases}NH_2\\COOH.\end{cases}$$

On being diazotized, treated with KCN, and hydrolysed, the above acid would give a dicarboxylic acid :—

$$C_6H_4\begin{cases}NH_2\\COOH\end{cases} \xrightarrow{NO.OH} C_6H_4\begin{cases}N_2Cl\\COOH\end{cases} \xrightarrow{KCN}$$

$$C_6H_4\begin{cases}CN\\COOH\end{cases} \xrightarrow{H.OH} C_6H_4\begin{cases}COOH\\COOH\end{cases}$$

The silver salt of this dicarboxylic acid should contain $\frac{216}{380} \times 100$ or 56·84 per cent of silver. This value agrees with that found experimentally, showing that our assumption as to the structure of the amino acid is correct.

Since the resulting dicarboxylic acid, when heated, yields an anhydride, the amino and the carboxyl groups in the given amino acid occupy *ortho* positions with respect to each other, *i.e.*, the acid possesses the structure,

$$C_6H_4\begin{cases}NH_2 & (1)\\COOH & (2).\end{cases}$$

Example 7. *An acid derived from p-xylene gave the following results on analysis :—*

0·162 *gm. gave* 0·4015 *gm.* CO_2 *and* 0·1430 *gm.* H_2O.

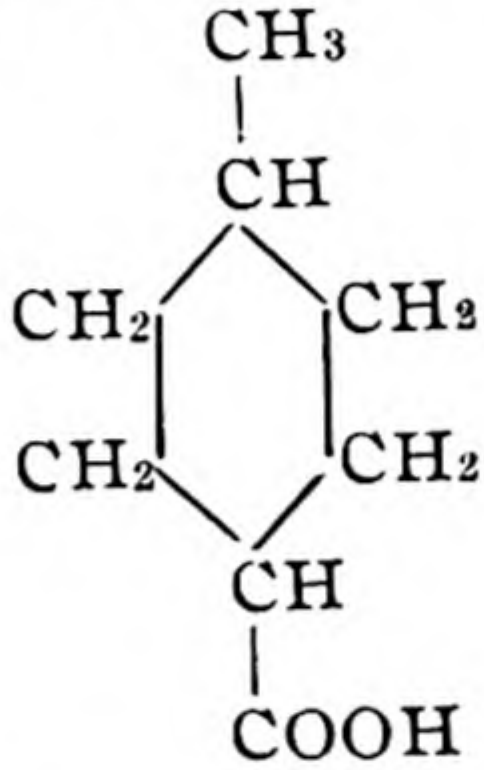
When treated with bromine it was converted into a bromo-derivative containing 36·2 *per cent of bromine, and this, when digested with alcoholic potash, yielded an acid which gave the following results on analysis :—*

0·17 *gm. gave* 0·4276 *gm.* CO_2 *and* 0·1309 *gm.* H_2O.

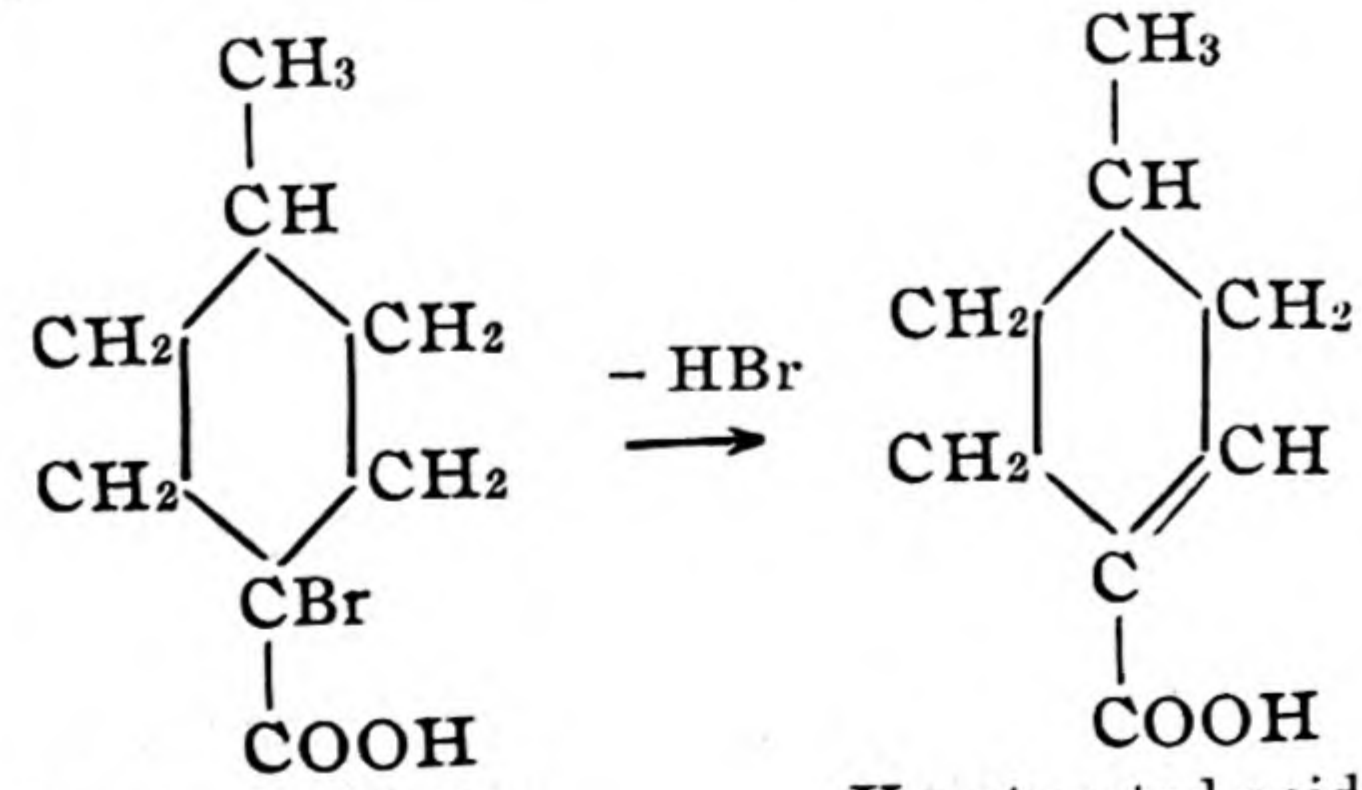
Assign constitutional formulae to these acids, stating your reason for their selection. (*Punjab B. Sc.* 1925.)

The *empirical formula* of the acid calculated as in the previous examples comes to C_4H_7O.

Since the acid is derived from *p*-xylene, C_8H_{10}, and since it must contain at least one carboxyl group, its molecular formula must be *twice* the empirical formula, *i.e.*, $C_8H_{14}O_2$. Its structure may be assumed to be:



As is well known, the carboxylic acids, when treated with bromine, give bromo-derivatives by the replacement of hydrogen in the *alpha* position to the carboxyl group. Since the above acid contains only one hydrogen atom attached to the carbon in the α-position, it must give a *mono*-bromo-derivative. This should theoretically contain $80 \times \frac{100}{221}$ or 36·3 per cent of bromine, which agrees with the experimental value. On treatment with alcoholic potash, a molecule of HBr would be eliminated as shown below :—

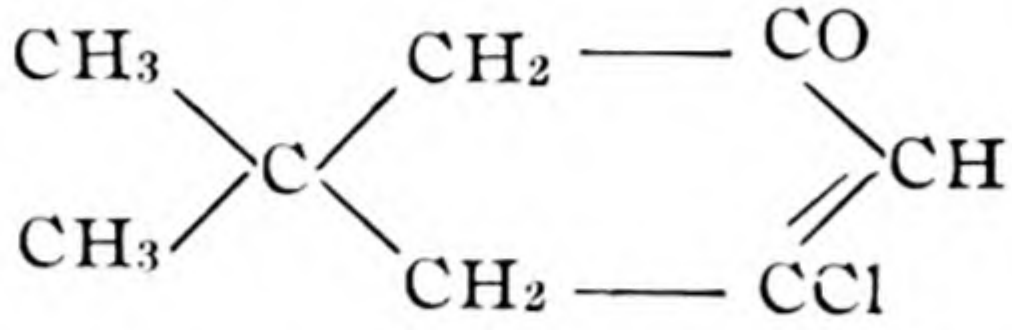


Bromo-derivative

Unsaturated acid

The empirical formula of this new acid calculated from the experimental data comes to C_4H_6O, which agrees perfectly with the formula deduced theoretically. Thus, we see that the above constitutional formulæ assigned to the three acids are fully supported by experimental facts.

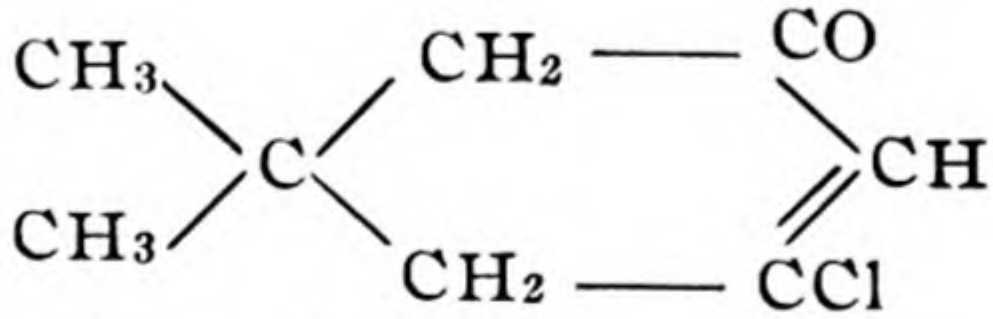
Example 8. *A ketone having the formula*



was reduced by means of sodium in absolute alcoholic solution; 0·1499 *gm. of the resulting compound (A) gave, on combustion,* 0·3835 *gm* CO_2 *and* 0·1559 *gm.* H_2O. *When treated with benzoyl chloride A was converted into a substance B, which contained* 73·75 *per cent of carbon and* 8·85 *per cent of hydrogen. What are the most probable formulae for A and B? Explain the reactions by which they were produced?* (*London Hons., Extl.*, 1907.)

The empirical formulæ of the compounds *A* and *B* calculated from the results of analysis are $C_5H_{10}O$ and $C_{17}H_{24}O_3$ respectively.

The original ketone, $C_8H_{11}OCl$, has the following structure:

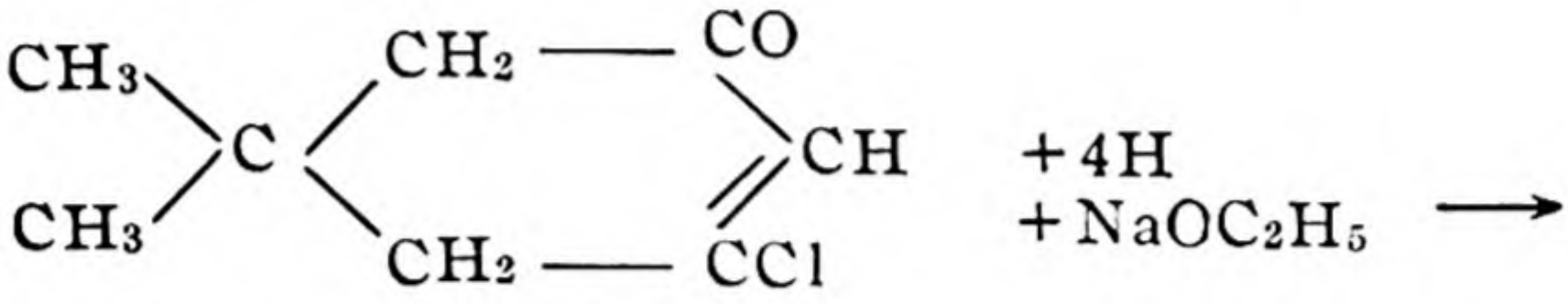


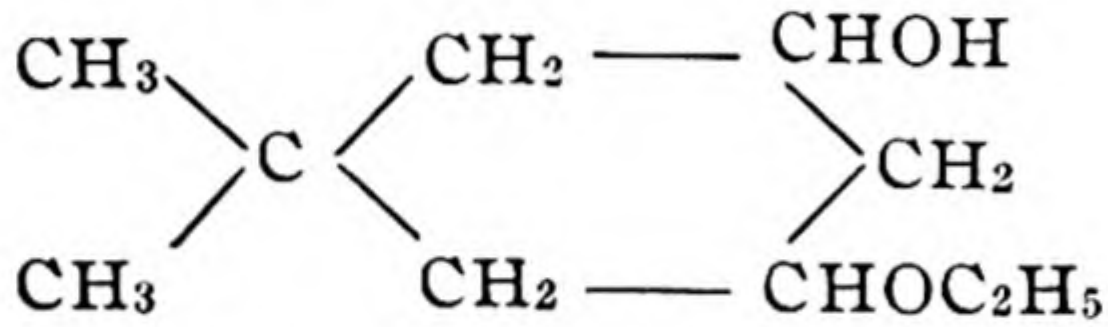
On treatment with sodium and absolute alcohol, it is evidently converted into $C_{10}H_{20}O_2$. Hence, we must assume—

(*i*) That the keto group has been replaced by a >CHOH group; this accounts for 2 additional atoms of hydrogen;

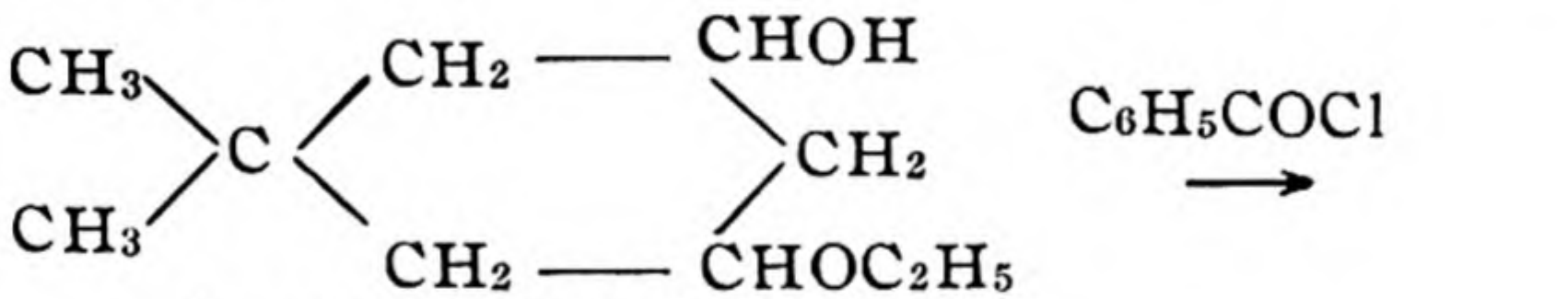
(*ii*) That the double bond is also attacked, with the addition of 2 more hydrogen atoms; and

(*iii*) That the chlorine linked to carbon has reacted with sodium ethoxide, C_2H_5ONa, yielding an ethoxy derivative; this accounts for the loss of a chlorine atom and the addition of one oxygen, two carbon, and five more hydrogen atoms. The complete change may be represented as follows:—

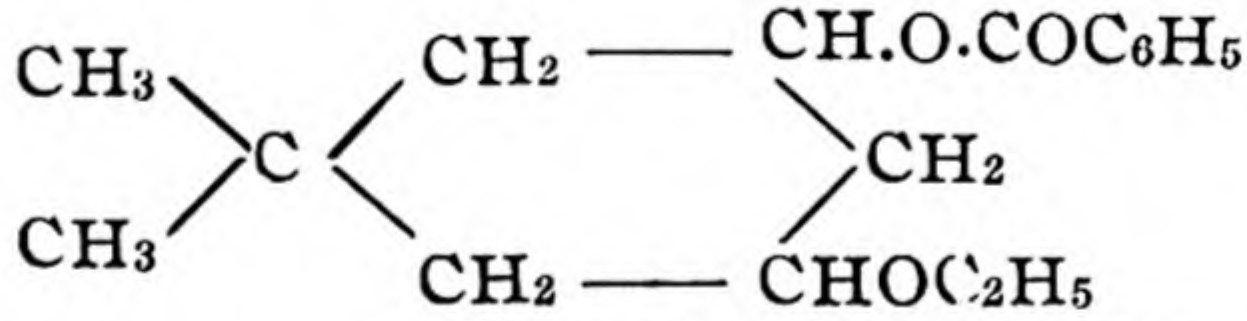




When treated with benzoyl chloride, *A*, $C_{10}H_{20}O_2$, gives *B*, $C_{17}H_{24}O_3$. This shows that the reagent brings about *benzoylation* of the secondary alcohol *A*, giving a benzoyl derivative *B*:—



Secondary alcohol (*A*)



Benzoyl derivative (*B*).

Example 9. *The monocyclic carbon compound A, containing only carbon, hydrogen, and oxygen, gave the following results on analysis:*

0·1120 *gave* 0·2638 CO_2 *and* 0·0720 H_2O. *When heated with ethyl alcohol and* 5 *per cent sulphuric acid, A was converted into a substance B, containing*

$C = 68·46$, $H = 8·67$.

When A was treated with bromine in chloroform solution, bromine was absorbed, hydrogen bromide evolved, and a compound, C, produced containing Br = 41·78 per cent. With hydroxylamine hydrochloride A gave a substance D, containing N = 19·84 per cent.

What information can you deduce from these data regarding the presence of any particular grouping in A, and what formula can you suggest which would be in accord with the observed facts? (*London Hons.* 1919.)

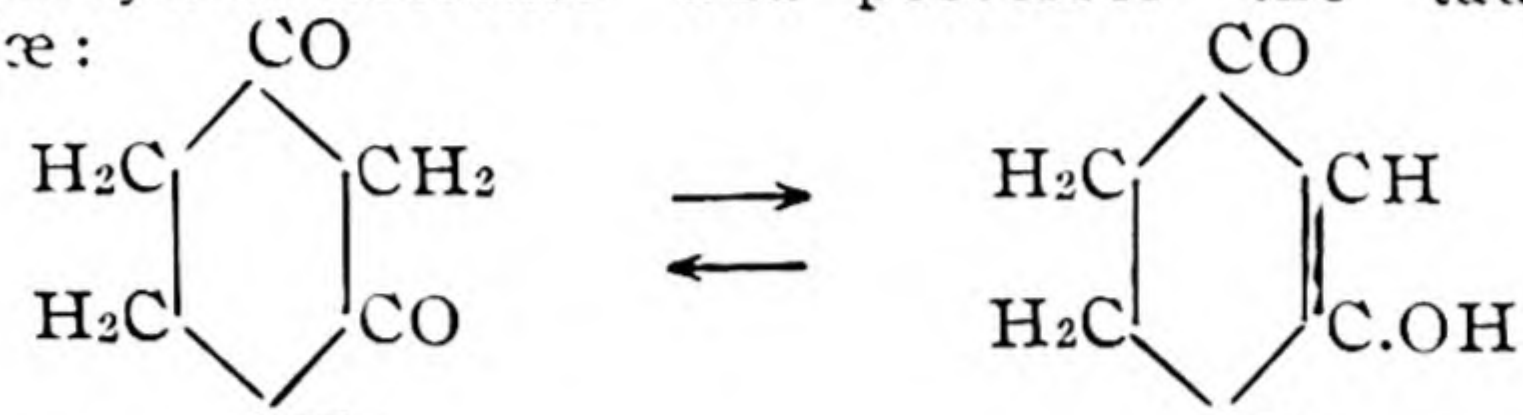
The empirical formulae of the compounds *A* and *B* calculated from the experimental figures are C_3H_4O and $C_8H_{12}O_2$ respectively.

If *C* were produced by the replacement of one atom of hydrogen of C_3H_4O by an atom of bromine, it would contain Br = 59·27, per cent, but actually it contains a lower proportion of bromine. Now, if we suppose that the molecular formula of *A* is *twice* its empirical formula, *i.e.* $C_6H_8O_2$, and that *C* is produced by the substitution of one atom of hydrogen by a bromine atom, it would contain 41·78 per cent of bromine, which agrees with the experimental value. Hence, the molecular formulæ of *A* and *C* must be respectively $C_6H_8O_2$ and $C_6H_7O_2Br$.

With ethyl alcohol and sulphuric acid *A* gives $C_8H_{12}O_2$ which is evidently a mono-ethoxy derivative of *A* [*i.e.* $C_6H_7O(OC_2H_5)$]. This shows that *A* contains one hydroxyl group.

If, on treatment with hydroxylamine, *A* had given rise to a *mon*oxime, the latter would possess the formula C_5H_8O (C:NOH) and would contain 11·03 per cent of nitrogen. If, on the other hand, a *di*oxime had been produced, it would possess the formula $C_4H_8(C{:}NOH)_2$ and would contain 19·72 per cent of nitrogen. This latter value agrees fairly closely with the experimental figure. Hence, evidently *A* contains two keto groups. But since it has also been shown to contain a hydroxyl group and has only *two* oxygen atoms, it must be a tautomeric substance, in which *one* of the ketonic groups gives rise to an enolic group.

Since the compound is monocyclic, and, further, since it is known that the keto-enol tautomerism is exhibited only by those cyclic compounds which contain the oxygen atoms linked to carbon atoms in the *meta* position to one another, we may conclude that the given compound *A* is dihydroresorcinol and possesses the tautomeric formulæ:



("Keto" form) ("Enolic" form)

Example 10. *An unsaturated ketone having the formula* $C_{10}H_{16}O$ *gave, on oxidation, a hydroxy acid of the formula* $C_9H_{18}O_3$. *This hydroxy acid, when oxidized with chromic acid gave a keto acid* $C_9H_{16}O_3$, *which, upon further oxidation with sodium hypobromite, gave α-isopropyl glutaric acid,* $COOH.CH_2.CH_2.CH(CH(CH_3)_2).COOH$

What constitution would you give to the ketone, the hydroxy acid, and the keto acid? (*Punjab M. Sc.* 1926.)

The final product of the above series of reactions is α-isopropyl glutaric acid ($C_8H_{14}O_4$):

$$COOH.CH_2.CH_2.CH(CH(CH_3)_2).COOH$$

This was obtained by the oxidation of a keto acid, $C_9H_{16}O_3$, which must evidently possess the structure I or II:—

I. $COOH.CH_2.CH_2.CH(CH(CH_3)_2).COCH_3$

II. $CH_3.CO.CH_2.CH_2.CH(CH(CH_3)_2).COOH$

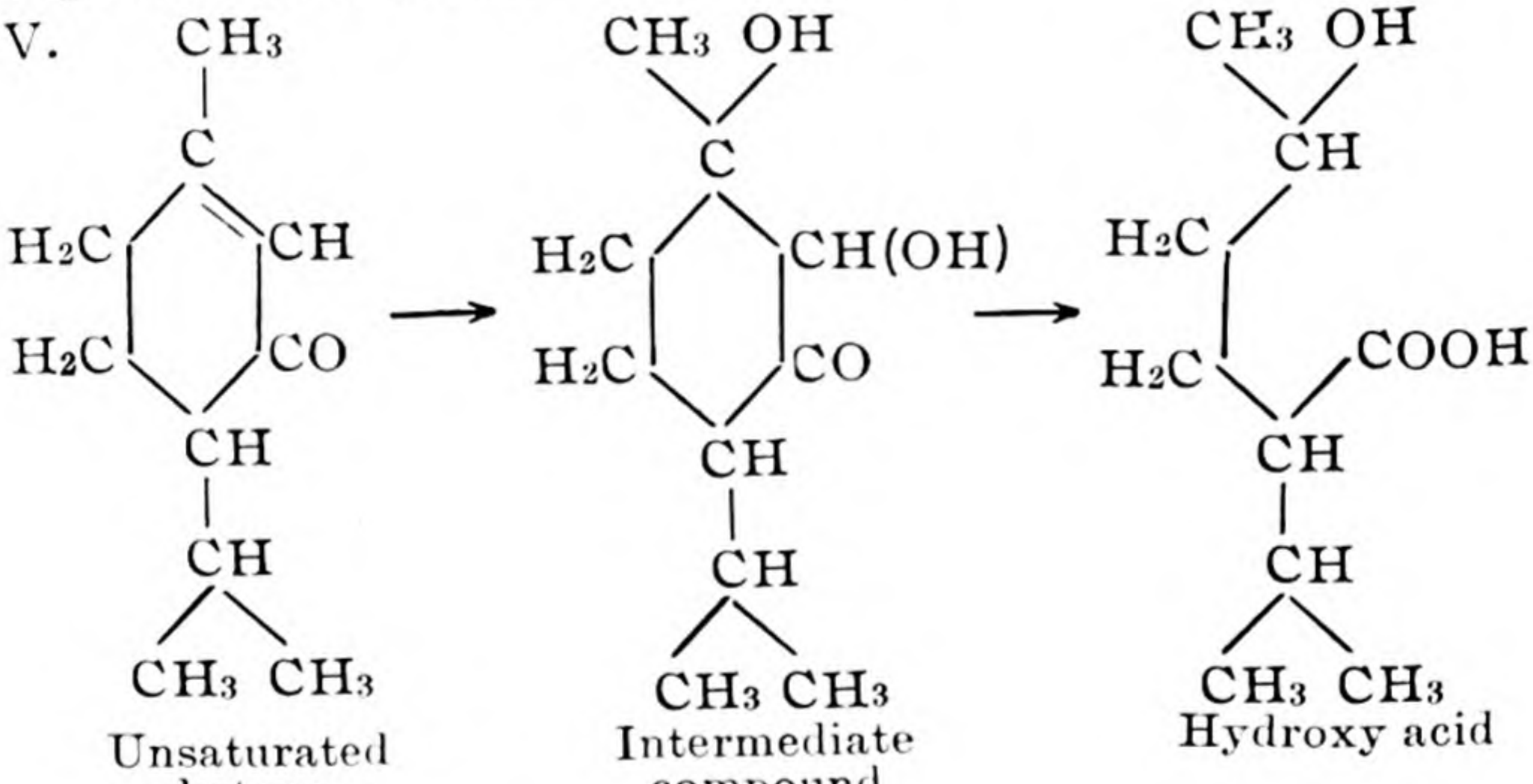
The keto acid, in turn, was produced by the oxidation of a hydroxy acid, $C_9H_{18}O_3$, which must possess the structure III or IV:—

III. $COOH.CH_2.CH_2.CH(CH.CH_3).CH(OH)CH_3$

IV. $CH_3.CH(OH).CH_2.CH_2.CH(CH.CH_3).COOH$

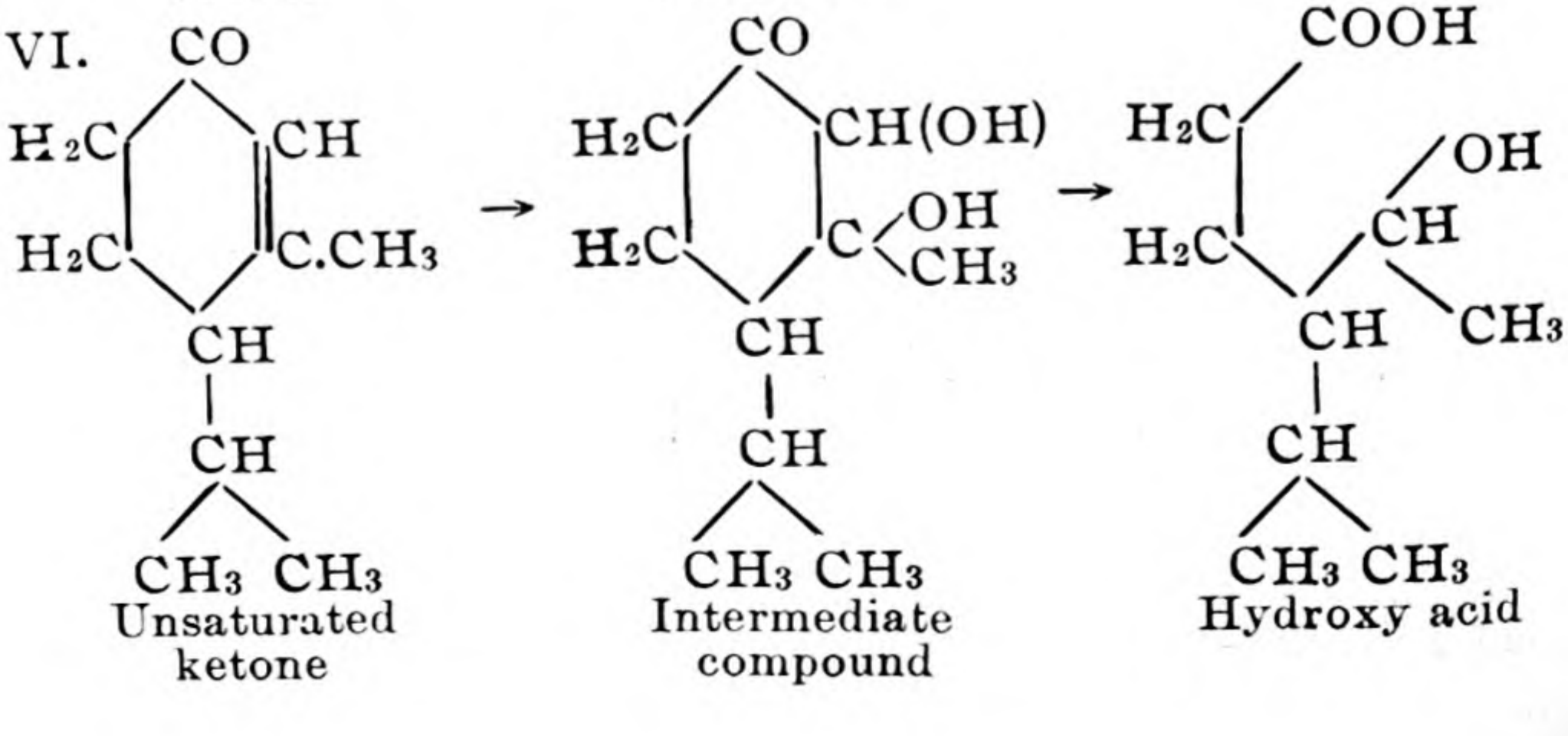
The hydroxy acid was obtained by the oxidation of an unsaturated ketone of the formula $C_{10}H_{16}O$. During this last reaction the double bond of the unsaturated ketone was evidently destroyed, one carbon atom was eliminated, while two hydrogen and two oxygen atoms were added. Assuming that the unsaturated ketone possesses either of the following constitutions, V or VI, the change may be represented as under :—

V.



Unsaturated ketone — Intermediate compound — Hydroxy acid

VI.



Unsaturated ketone — Intermediate compound — Hydroxy acid

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Thus we see that the unsaturated ketone may be regarded as a derivative of a terpene. Of the two alternative constitutions that we are here led to propose, the *first* one, *i.e.* V, appears to be by far the more probable, since only the terpenes derived from *p*- and *m*-cymenes are known. The hydroxy and the keto acids must therefore possess the structures III and I given above.

EXERCISES

1. An organic compound containing only carbon, nitrogen and hydrogen was found on combustion to contain 53·33 per cent of carbon. To estimate nitrogen 0·150 gm. of the substance was kjeldahlised and the ammonia produced required for neutralisation 33·3 c.c. of N/10 HCl. The vapour density compared with hydrogen was found to be 22·5. Calculate the molecular formula of the compound.

2. 0·37 gm. of a substance containing carbon, hydrogen, and oxygen gave on combustion 0·66 gm. of CO_2 and 0·27 gm. of water. Further, 0·123 gm. of the substance displaced 39·6 c.c. of air at 17°C. and 760 mm. in a determination of its vapour density by the Victor Meyer method. Ascertain from these data the molecular formula of the substance. (*Inter. B.Sc. Manc.*, 1906.)

3. An organic substance having the following percentage composition :—

$$C = 65{\cdot}77\%,\ H = 15{\cdot}00\%,\ N = 19{\cdot}10\%$$

gave on treatment with $NaNO_2$ and HCl an oily liquid containing 27·4 per cent of nitrogen. The vapour densities of the original compound and the oily liquid as determined by Victor Meyer's method are 36·5 and 51 respectively. Write possible structural formulæ of the original substance. (*K. C. III Year*, 1930.)

4. An organic substance gave the following results on analysis :—

0·2167 gm. gave 0·3223 gm. CO_2 and 0·1650 gm. H_2O. By the Kjeldahl method 0·531 gm. required 9 c.c. of normal Sulphuric acid for neutralisation of the ammonia.

When the original substance was boiled with NaOH, ammonia was evolved, and the dry residue when heated with Soda-lime gave methane. What was the original substance? Explain the above reactions.

(*Punjab B. Sc.*, 1922. *B.Sc. Hons.* 1915.)

5. An organic compound of the formula C_8H_{10} yields, on oxidation, a colourless crystalline dibasic acid containing 57·8 per cent carbon and 3·6 per cent hydrogen. The silver salt contains 56·8 per cent silver. On heating the acid, it is converted into a compound of the formula $C_8H_4O_3$, and, on distillation with lime, benzene is formed. Discuss the structure of the original compound. (*Punjab B.Sc.* 1929.)

6. Assign a structure to a compound which gave the following results on analysis :—

(*a*) 0·130 gm. yielded on combustion, 0·264 gm. CO_2 and 0·090 gm. H_2O.

(*b*) 0·130 gm. heated in Victor Meyer's apparatus displaced 26 c.c. of air measured at 21°C and 710 mm.

(*c*) When heated with ammonia, it yielded propionamide. (*Punjab B.Sc.* 1924.)

7. An acid derived from *p*-xylene gave the following results on analysis :—

0·162 gm. gave 0·4015 gm. CO_2 and 0·1430 gm. H_2O.

When treated with bromine it was converted into a bromo-derivative containing 36·2 per cent bromine, and this, when digested with alcoholic potash, yielded an acid which gave the following results on analysis :—0·17 gm. gave 0·4276 gm. CO_2 and 0·1309 gm. H_2O. Assign constitutional formulæ to these acids, stating your reasons for their selection.

(*Manchester B.Sc. Hons.* 1905; *Punjab B. Sc.* 1925.)

8. The analysis of an organic substance gave the following results: 0·2115 gm. on combustion gave 0·4655 gm. CO_2 and 0·2533 gm. H_2O. The vapour density of the substance was 29·7. Calculate the molecular formula and give the names of the substances possessing this formula. (*London Inter.* 1908.)

9. 0·228 gm. of a substance, containing C, H, and O, gave on combustion 0·396 gm. CO_2 and 0·324 gm. H_2O. What is the simplest formula of the substance? By what tests would you determine its nature?

10. Two liquids, one boiling at 83°C. and the other at 57°, gave, on analysis, the same results, *viz.*, 0·2376 gm. gave, on combustion, 0·2112 gm. CO_2 and 0·0864 gm. H_2O; 0·121 gm. gave, when heated with silver nitrate and nitric acid, 0·351 gm. Ag Cl. Calculate the simplest formula for these substances. How do you account for two substances having the same composition, and what do you regard as the true formula of each compound?
(*London Inter. Hons.* 1904.)

11. An aliphatic dicarboxylic acid gave the following results on analysis:—

0·1072 gm. gave 0·1408 gm. CO_2 and 0·0432 gm. H_2O. What is the acid?

12. 0·2797 gm. of a liquid hydrocarbon gave, on combustion, 0·9364 gm. CO_2 and 0·2190 gm. H_2O. The vapour density of the hydrocarbon was found to be 46. On oxidation, it yielded an acid having the empirical formula $C_7H_6O_2$. What is the hydrocarbon?

13. The ammonium salt of a non-nitrogenous organic acid gave the following results on analysis: 0·2856 gm. gave 0·3102 gm. CO_2 and 0·180 gm. H_2O; 0·1562 gm. gave 22·1 c.c. of dry nitrogen at 13°C, and 779 mm. pressure. Find the simplest formula of the salt and also that of the acid. (*London Hons. Extl.* 1907.)

14. An oily liquid with a pleasant fruity odour was found, on analysis, to contain C = 54·6% and H = 9·1%. Its vapour density was found to be 44. On heating with caustic potash solution and distilling, a distillate was obtained which gave the iodoform reaction. The residual liquid in the distilling flask, on treatment with excess of sulphuric acid and distilling yielded a distillate, which, after exact neutralisation with ammonia, gave a deep red coloration with ferric chloride. What was the original liquid?

15. Two liquids, one with a vapour density 15 and the other 30, were found, on analysis, to possess the same percentage composition, *viz.* C = 40·0°/₀, H = 6·7°/₀ and O = 53·3°/₀. The first liquid gave the silver mirror test, but had no effect on sodium carbonate. The second decomposed sodium carbonate with evolution of CO_2, but it had no effect on ammoniacal silver solution. What were the two liquids ?

16. A colourless crystalline solid was found to contain C = 71·1°/₀, H = 6·7°/₀, N = 10·4°/₀. On boiling the substance with concentrated hydrochloric acid and adding an excess of KOH, an oily liquid was obtained, which gave a violet coloration with a solution of sodium hypochlorite. What was the original subtance ?

17. Two aromatic substances, one soluble in aqueous KOH and the other insoluble, are found, on analysis, to possess the same percentage composition, *viz.* C = 77·8 per cent., H = 7·4 per cent., and O = 14·8 per cent. What are the substances ?

18. A gaseous hydrocarbon (density = 21) is found to contain 85 per cent of carbon. On treatment with bromine, it gave a colourless oil containing C = 17·8 per cent, H = 3·0 per cent. Write the structural formulæ of the hydrocarbon and also that of the bromo compound.

19. An organic liquid containing only C, H and O gave the following results on analysis. 2·1542 gm. of the substance gave 0·3082 gm. CO_2 and 0·1262 gm. H_2O. The vapour density of the substance was found to be 44. Several different substances would give results in agreement with these figures. Indicate what these substances might be and outline methods for distinguishing them from one another. (*Trinity Group, Cambridge.*)

20. 0·2881 gm. of an alcohol, on being added to methyl magnesium iodide, caused the evolution of 48·33 c.c. of methane measured at 20° and 755 mm. Calculate the molecular weight of the alcohol.

21. A substance gave the following result on analysis :—

0·2500 gave 0·6027 CO_2 and 0·339 H_2O.

0·2000 gave 33·4 c.c. of nitrogen at 20° and 750 m.m. Its vapour density compared with hydrogen was 37. Calculate the composition of the substance and give the constitutional formulæ of the possible substances of this composition. (*Board of Education*, 1907.)

22. A substance on analysis gave C = 40·57, H = 8·53, and N = 23·65 per cet. This substance was treated with bromine and caustic potash solution; the product was found to yield a salt with hydrochloric acid and to evolve nitrogen with nitrous acid. Assign a formula to the substance. (*Peterhouse Group, Cambridge.*)

23. On combustion, 0·357 gm. of an organic compound, A, gave 0·561 gm. of CO_2 and 0·077 gm. of water. The compound contains 16·7 per cent of nitrogen. On reduction it gave a derivative, B, having the following percentage composition: C = 52·2, H = 4·35, N = 20·3, O = 23·15. The compound, B, forms a hydrochloride containing 20·92 per cent of hydrochloric acid. Find the formulae of A and B. (*Punjab B. Sc. Hons.* 1926.)

24. Certain white crystals having, in aqueous solution, a strongly acid reaction were found to consist of H = 4·76, C = 19·05, O = 76·19 per cent; what is the simplest formula which would express the results of the analysis? Is this the formula adopted for the compound? If not, why not? (*London B. Sc. Pass, Extl.*, 1904.)

25. An oxidation product of glycerol was found to contain 40 per cent of carbon and 6·7 per cent of hydrogen. 0·3 gm. of the compound dissolved in 50 c.c. of water depressed the freezing point by 0·12°C. Determine the molecular weight of the compound, the cryoscopic constant of water being 18·6°C. Suggest constitutional formulae for two isomeric compounds which might be obtained in this way, both of which yield the same osazone. (*Downing College, Cambridge.*)

26. An organic substance gave the following results on analysis :—

0·2167 gm. gave 0·3223 gm. CO_2 and 0·1650 gm. H_2O. By the Kjeldahl method 0·531 gm. required 9 c.c. of normal sulphuric acid for neutralization of the ammonia.

When the original substance was boiled with sodium hydroxide, ammonia was evolved, and the dry residue when heated with soda lime gave methane. What was the original substance ? (*Punjab B. Sc.* 1922.)

27. When sodium is dissolved in methyl alcohol and the solution is heated with chloroform, a liquid compound is formed, containing 45·3% of carbon and 9·4% of hydrogen, the rest being oxygen. Heated with dilute sulphuric acid this liquid yields formic acid. What information concerning the constitution of formic acid can be obtained from these facts ?

(*Peterhouse Group, Cambridge.*)

28. A substance consisting of C, H and O only gives on analysis, C = 68·19% and H = 13·64%. When gently oxidized it is converted into a substance which gives C = 69·77% and H = 11·63%. The latter on further oxidation under suitable conditions gives a mixture which on analysis is found to consist of saturated fatty acids containing one, two, three and four atoms of carbon per molecule, but none of the higher acids. Suggest a constitutional formula for the substance and describe the tests you would employ to confirm it.

(*Pembroke College, Cambridge.*)

29. A pleasant-smelling liquid with a vapour density of 44, contained C = 54·6% and H = 9·1% the remainder being oxygen. When decomposed with hot sodium hydroxide solution and distilled, it yielded a distillate which gave the iodoform reaction, whilst the residue in the distilling flask, after careful neutralization, gave a deep-red coloration with ferric chloride solution. Determine the structural formula of the original substance.

(*Liverpool B. Sc.*)

30. Determine the molecular formula of a compound from the following experimental results : 4·1 c.c. of the gas were mixed with 10·8 c.c. of oxygen and exploded by an electric spark, the volume of the gaseous products being 14·9 c.c. On adding KOH there was a contraction of 8·2 c.c. and a further contraction of 2·6 c.c. followed on adding pyrogallol, the residue being nitrogen. Describe

how the compound may be prepared and give a brief account of its properties. (*Downing College, Cambridge.*)

31. Calculate the formula of the aliphatic dicarboxylic acid which gave the following results on analysis :—

0·1340 gave 0·1760 CO_2 and 0·0540 H_2O.

(*Lond. Scholarships* 1910.)

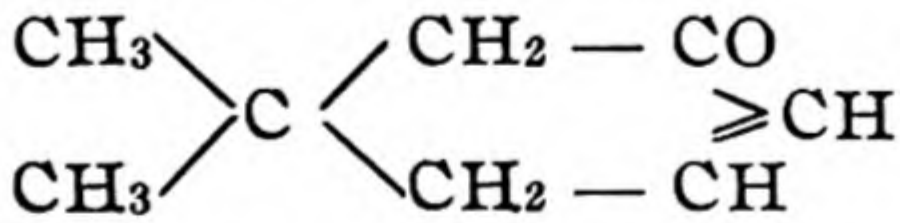
32. An organic compound (C = 39·13 ; H = 8·69%) gave on treatment with nitric acid—a dibasic acid, with strong sulphuric acid—an unsaturated aldehyde, with hydrochloric acid gas in acetic acid—a secondary alcohol, and with PCl_5—a chlorinated hydrocarbon. What was the original compound ? (*Allahabad M. Sc.* 1930.)

33. A compound of carbon, hydrogen, and oxygen gave the following results on combustion :—

0·146 gm. gave 0·374 gm. CO_2 and 0·154 gm. of H_2O. Vapour density (H = 1) = 42. The compound reacts with hydroxylamine and phenylhydrazine, but not with acetyl chloride. On oxidation it gives a mixture of acetic and propionic acids with traces of other acids. Determine the molecular weight and structural formula of the compound. (*Punjab B. Sc. Agr.* 1224.)

34. 0·4185 gm. of the calcium salt of an organic acid (containing C, H and O) gave on ignition 0·1349 gm. of $CaCO_3$. When the calcium salt was heated in a distilling flask, there distilled over a substance which gave on analysis C = 85·7, H = 6·7. Both this substance and the original acid gave benzoic acid on oxidation. Suggest a formula for the acid. (*Pembroke College, Cambridge.*)

35. A substance of the formula



on oxidation with potassium permanganate gave a product which was analyzed with the following results :—

O·111 gave 0·2142 CO_2 and 0·0654 H_2O.

0·2019 required 12·85 c.c. of N/10 NaOH for neutralization in the cold and a further 11·9 c.c. on warming.

What structural formula would you assign to this oxidation product? (*London Hons., Extl.*, 1908.)

36. An organic substance is found to contain C = 52·2%, H = 13%, O = 34·8%, and its molecular weight is 46. It reacts neither with sodium nor with PCl_5. What is the substance?

37. The ethyl ester of a dibasic acid, to which a normal carbon chain is assigned, has the composition: C = 61·11, H = 9·26, O = 29·63 per cent. When heated at 120° with sodium and a trace of alcohol, this ester is converted into a substance *A* of the composition: C = 63·53, H = 8·23, O = 28·24 per cent. From *A*, when boiled with dilute sulphuric acid, a second substance *B* is obtained of the composition: C = 73·47, H = 10·20, O = 16·33 per cent, the oxime of which contains N = 12·39 per cent. What is the probable constitution of *B*?

(*London B. Sc. Hons.* 1911.)

38. 0·2736 gm. of a monobasic organic acid, *A*, required 18·00 c.c. of N/10 barium hydroxide. The sodium salt of *A*, when heated with soda lime, gave a volatile liquid, *B*. 0·1070 gm. of *B*, on being decomposed with HI (Zeisel's method), gave a sufficient amount of methyl iodide to precipitate 0·2327 gm. AgI, the residual product was found to be phenol. What constitutional formulæ would you assign to *A* and *B*?

39. A sample of commercial butyl mercaptan weighing 0·300 gm. required for oxidation 31·2 c.c. of N/10 iodine. Calculate its purity.

40. 0·3074 gm. of an ester required for its hydrolysis 26·47 c.c. of N/10 alcoholic KOH. The silver salt from the acid of the ester was found to contain 59·63 per cent of silver. What ester was it?

41. 0·500 gm. of a sample of commercial ethyl acetate was boiled with 30 c.c. of N/5 alcoholic KOH. For back titration 14·5 c.c. of N/10 HCl was required. Calculate the percentage purity of the ester.

42. The combustion of 0·246 gm. of a liquid hydrocarbon yielded 0·792 gm. of carbon dioxide and 0·270 gm.

of water. The hydrocarbon absorbed bromine readily, and yielded a compound containing 79·6 per cent of bromine. From these data, what conclusions do you draw as to the formula and the nature of the hydrocarbon?

(*London Inter.* 1909.)

43. In a Zeisel's determination for methoxyl groups one gm. of a substance of the formula $C_3H_8O_2$ gave after treatment with red phosphorus, iodine and water, and the decomposition of the resulting methyl iodide with alcoholic silver nitrate 2·67 gm. of AgI. Calculate how many methoxy groups are present in the molecule.

(*Punjab B. Sc. Hons.* 1914.)

44. A compound has the following percentage composition :—

C = 81·55; H = 4·8; N = 13·6.

Its vapour density is 51·15. Calculate the molecular formula.

It evolves ammonia on boiling with potash. The original substance on reduction with sodium and alcohol forms a base which reacts with nitrous acid giving off nitrogen and yielding an alcohol. The alcohol can be oxidized to benzoic acid. What is the original substance?

(*Punjab B. Sc. Hons.* 1920.)

45. An organic compound containing the aldelhydic group was acted upon with hydroxylamine and the resulting oxime analysed.

It gave the following composition :—

Carbon	69·4%
Hydrogen	5·7%
Oxygen	13·2%
Nitrogen	11·6%

What is the probable formula of the compound? How are the above-mentioned chemical processes carried out?

(*Punjab M.Sc.* 1913.)

46. A dibasic acid containing only carbon, hydrogen, and oxygen was found by analysis to contain C, 26·7 per cent; H, 2·2 per cent.

A determination of the vapour density of its dimethyl ester gave $\triangle = 59$. What is the acid? (*Manc. Inter.* 1910.)

47. A ketoxime, on analysis, was found to possess the following composition :-–

Carbon, 55·2; hydrogen, 10·3; nitrogen, 16·1 per cent. What is the formula of this compound and from what ketone is it derived? (*Board of Education* 1910.)

48. A compound having the percentage composition C, 68·7; H, 5·2; N, 8·0 forms salts with acids and with strong (but not with weak) bases, and appears to be a saturated body. Zeisel's determination indicates one methyl group. Suggest the nature of the substance and plan a scheme for its further elucidation.

(*Allahabad M.Sc.* 1930.)

49. A dibasic acid gave, on analysis, the following results: 0·1740 gm. gave 0·3388 gm. CO_2 and 0·1008 gm. H_2O. When it was treated with bromine it yielded dibromo derivative which gave, on analysis, C = 26·4, H = 3·2, Br = 50·3. Oxidation with permanganate converted the dibasic acid into dimethyl malonic acid and oxalic acid. What is the constitution of the acid? (*Manch. B. Sc. Hons.* 1906.)

50. A ketone of a dicylic terpene, 0·152 grams in weight when dissolved in 50 grams of benzene showed 0·1°C as the depression of the freezing point. On oxidation, the ketone gave a dibasic acid the anhydride of which gave the following results on analysis :—0·091 grams of the substance gave 0·22 grams CO_2 and 0·063 grams H_2O. This anhydride on reduction with sodium amalgam produced a substance, A, which on analysis gave C = 71·43% and H = 9·52%.

On treatment with KCN, the substance, A, gave a nitrile of a potassium salt of the formula $C_{11}H_{16}O_2NK$. This nitrile when hydrolysed produced a dibasic acid, B, which on combustion gave C = 61·69% and H = 8·41%. The calcium salt of, B, gave the original ketone on distillation.

What conclusions would you draw with regard to the probable constitution of the various substances? (When a gram molecule is dissolved in 100 grams of benzene, depression of freezing point = 50°C.) (*Punjab M. Sc.* 1928.)

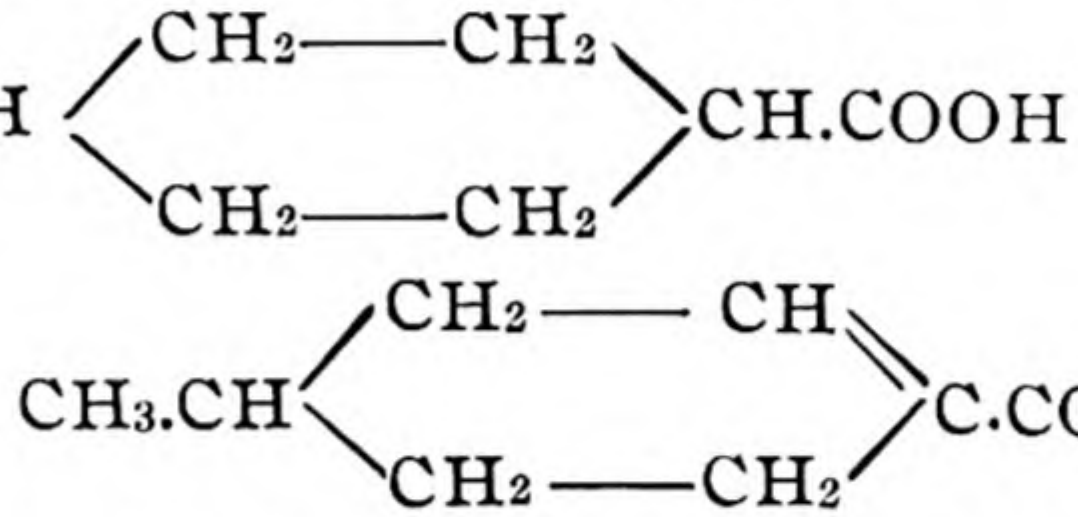
Answers.

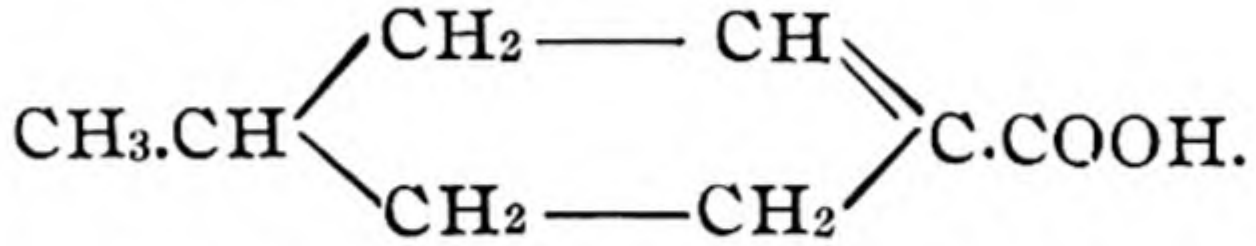
1. C_2H_5N. **2.** $C_3H_6O_2$.

3. $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>NH$; $\begin{matrix}CH_3\\C_3H_7\end{matrix}>NH$. **4.** Acetamide, CH_3CONH_2.

5. *o*-Xylene, $C_6H_4(CH_3)_2$.

6. Propionic anhydride, $(C_2H_5CO)_2O$.

7.




8. C_3H_8O; propyl alcohol, isopropyl alcohol, methyl ethyl ether.

9. CH_4O. **10.** CH_2Cl. $\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}$ and $\begin{matrix}CH_3\\|\\CHCl_2.\end{matrix}$

11. Malic acid, $\begin{matrix}CH(OH)COOH\\|\\CH_2COOH.\end{matrix}$

12. Toluene, $C_6H_5CH_3$.

13. $C_3H_4(OH)(COONH_4)_3$.
$C_3H_4(OH)(COOH)_3$, *i.e.* Citric acid.

14. Ethyl acetate, $CH_3COO.C_2H_5$.

15. Formaldehyde, HCHO; and acetic acid, CH_3COOH.

16. Acetanilide, $C_6H_5.NH.CO.CH_3$.

17. (*i*) *o*-, *m*-, or *p*-cresol, $C_6H_4(CH_3)OH$.
(*ii*) Benzyl alcohol, $C_6H_5CH_2OH$.

18. $CH_2:CH.CH_3$ and $CH_2.Br.CHBr.CH_3$.

19. $C_4H_8O_2$; butyric and isobutyric acids, $CH_3.CH_2CH_2.COOH$, $CH_3.CH(CH_3)\,COOH$; methyl propionate; $C_2H_5COOCH_3$; ethyl acetate $CH_3COOC_2H_5$; propyl and isopropyl formates, $HCOO.C_3H_7$, $HCOO.CH(CH_3)_2$.

20. 144.

21. $C_4H_{11}N$;

$CH_3.(CH_2)_3.NH_2$, $(CH_3)_2.CH.CH_2.NH_2$, $(CH_3)_3.C.NH_2$,

$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>NH$, $\begin{matrix}CH_3.CH_2.CH_2\\CH_3\end{matrix}>NH$, $\begin{matrix}(CH_3)_2CH\\CH_3\end{matrix}>NH$,

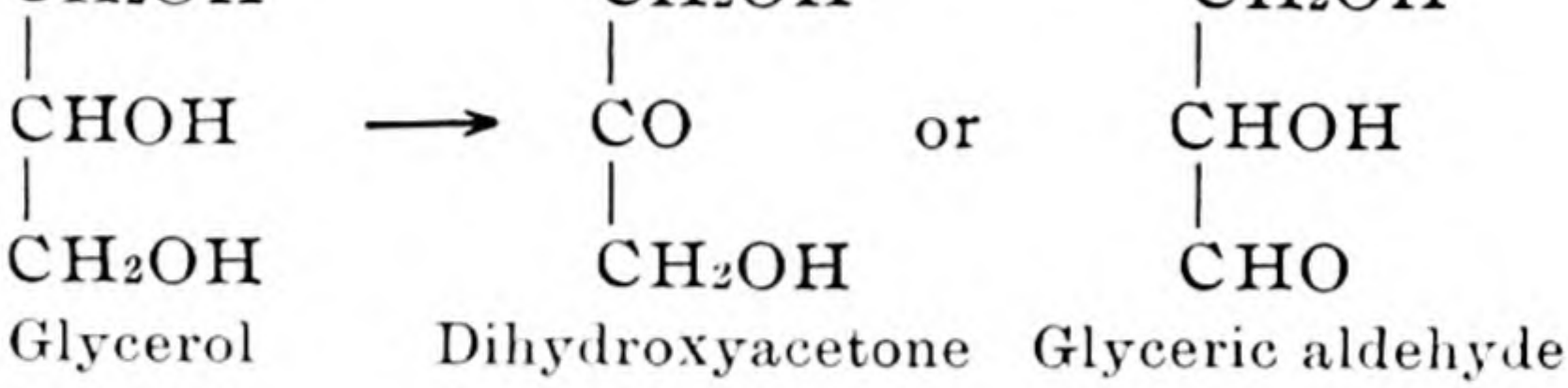
$(CH_3)_2NC_2H_5$.

22. CH_3CONH_2.

23. $A=C_6H_4<\begin{matrix}NO_2\\NO_2\end{matrix}$; $B=C_6H_4<\begin{matrix}NO_2\\NH_2\end{matrix}$

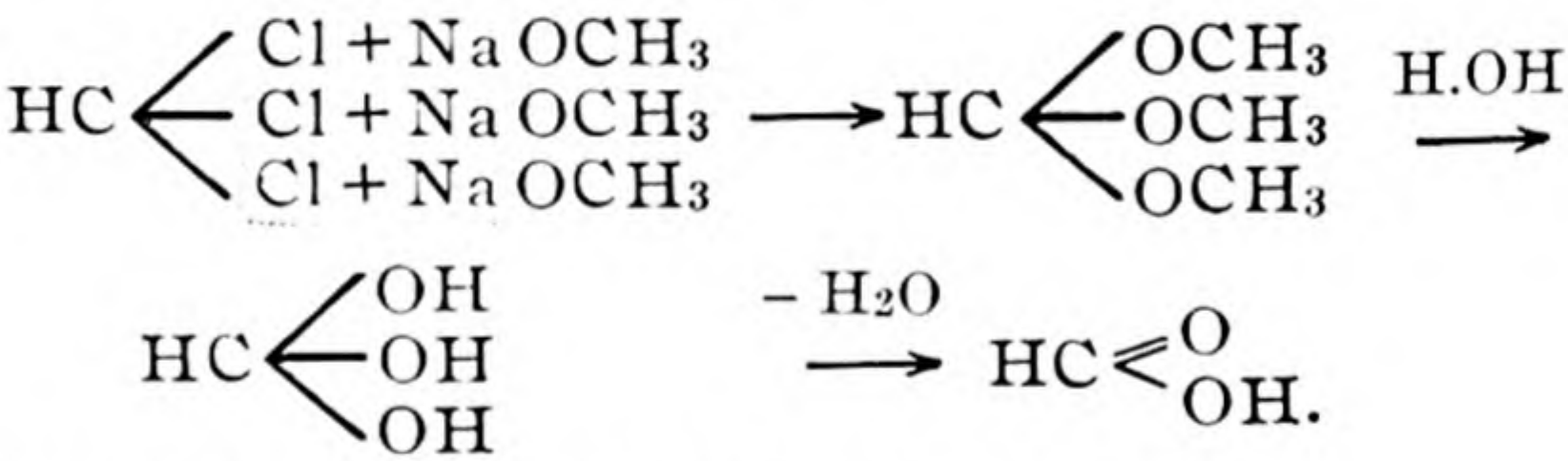
24. CH_3O_3. The adopted formula is $(COOH)_2.2H_2O$.

25.



26. Acetamide, $CH_3\,CONH_2$.

27.



28. Secondary alcohol $CH_3.CHOH.C_3H_7$ ⟶

$CH_3.CO.C_3H_7$ (ketone).

29. $CH_3COOC_2H_5$. **30.** $(CN)_2$.

31. $COOH.CH_2.CH(OH)COOH$, malic acid;

$CH_3.C(OH).(COOH)_2$, isomalic acid;

$CH_2OH.CH.(COOH)_2$, β-hydroxy isosuccinic acid

32. Glycerol, $CH_2OH.CHOH.CH_2OH$.

33. 86; $CH_3.CO.CH_2.CH_2.CH_3$.

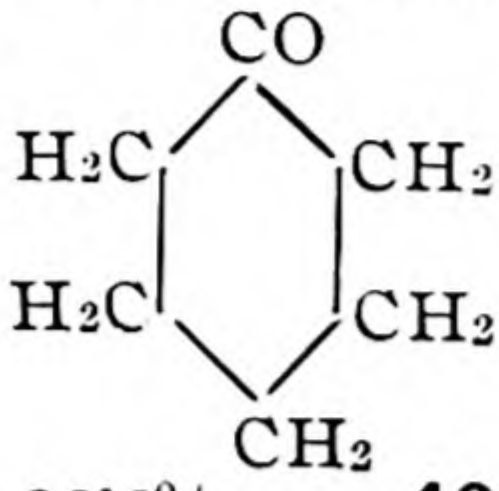
34. $CH_3.C_6H_4COOH$; distillate, $CH_3.C_6H_4.CO.C_6H_4CH_3$.

35. $COOH.CH.C(CH_3)_2.CH_2.CO$.

$\quad\quad\quad

36. Dimethyl ether, $(CH_3)_2O$.

37.



38. A, $CH_3O.C_6H_4.COOH$
B, $C_6H_5.O.CH_3$.

39. 93·6%. **40** Propyl propionate. **41.** 80·1%.

42. C_6H_{10}; a di-olefine or acetylene hydrocarbon.

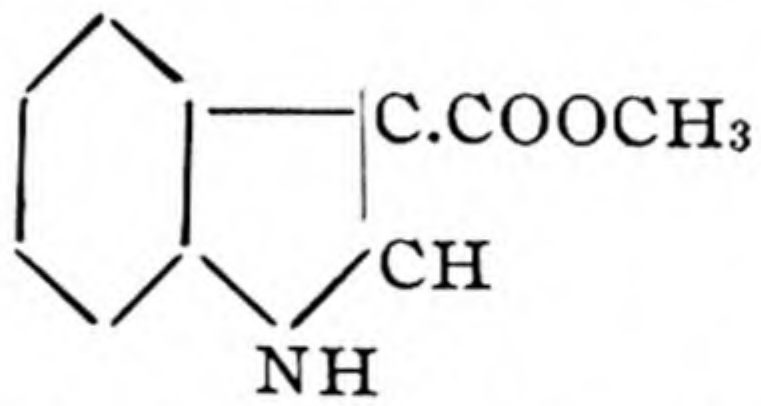
43. One methoxy group.

44. C_7H_5N; Benzo-nitrile, C_6H_5CN.

45. $C_6H_5.CHO$. **46.** Oxalic acid.

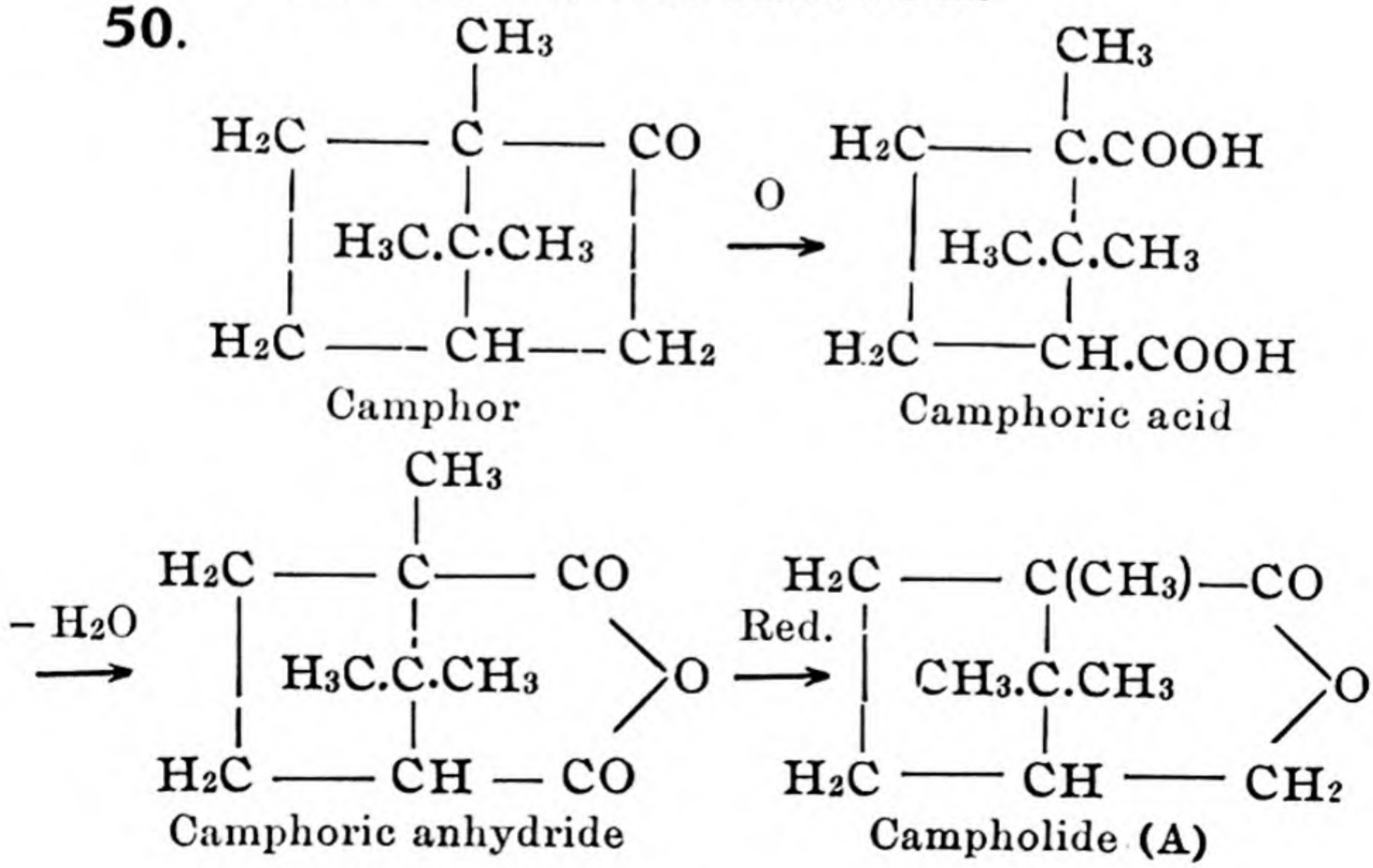
47. $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!C{:}NOH$; from methyl ethyl ketone.

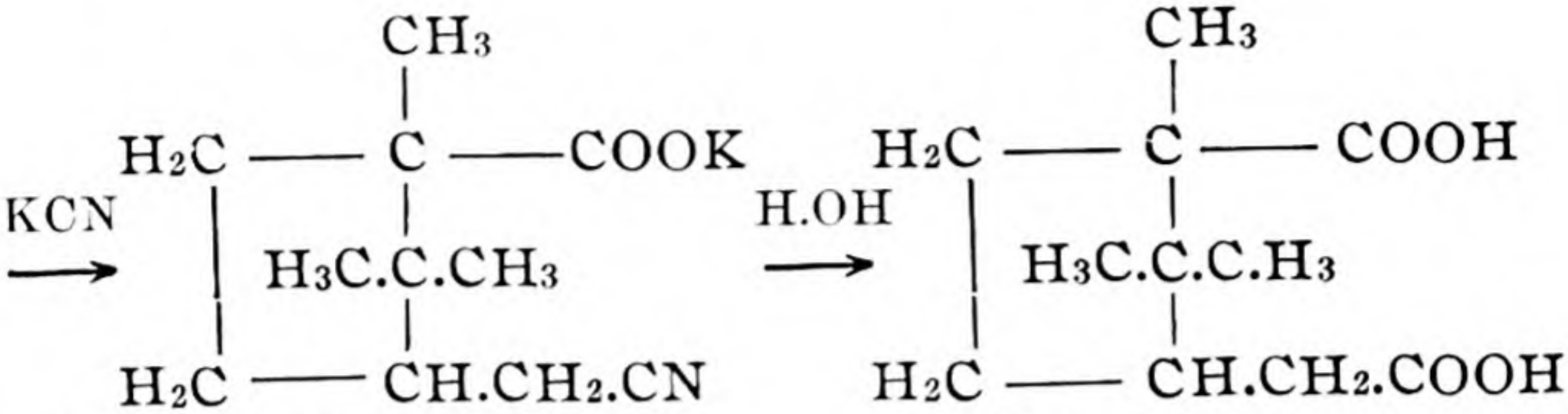
48.



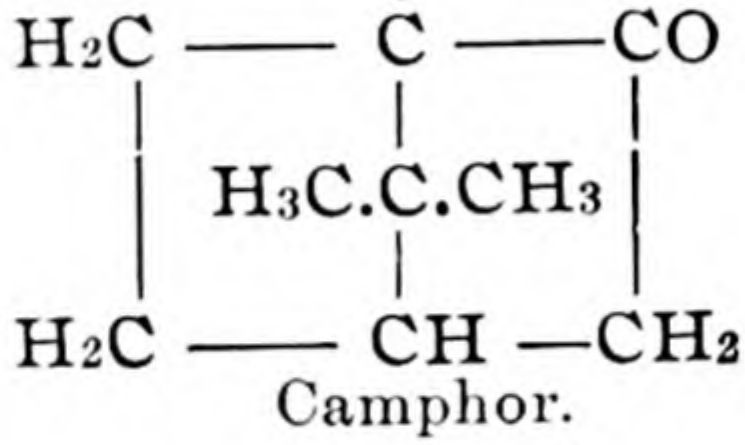
49. *aa*-Dimethyl glutaconic acid,
$COOH.C(CH_3)_2.CH{:}CH.COOH$.

50.





Distil the calcium salt →



CHAPTER II

THE GASEOUS STATE

6. Relation between Molecular Weight and Vapour Density. The *vapour density* of a substance is the ratio between the weight of a certain volume of its vapour to the weight of the same volume of hydrogen under the same conditions of temperature and pressure. Or,

$$\text{V. D.} = \frac{\text{Wt. of a certain volume of vapour}}{\text{Wt. of the same volume of hydrogen}}$$

$\therefore$ By Avogadro's Hypothesis—

$$\text{V. D.} = \frac{\text{Wt. of } n \text{ molecules of the vapour}}{\text{Wt. of } n \text{ molecules of hydrogen}}$$

$$= \frac{\text{Wt. of 1 molecule of the substance}}{\text{Wt. of 1 molecule of hydrogen}}$$

Since the hydrogen molecule is diatomic, the above relation becomes—

$$\text{V. D.} = \frac{\text{Wt. of 1 molecule of the substance}}{2 \times \text{Wt. of 1 atom of hydrogen}}$$

$$\text{Or, } 2 \times \text{V. D.} = \frac{\text{Wt. of 1 molecule of the substance}}{\text{Wt. of 1 atom of hydrogen}} = \text{M.W.}$$

Hence the *molecular weight of a substance in the gaseous state is twice its vapour density.*

7. Determination of Vapour Densities of Gases. The vapour densities of gases are determined by the following two methods:—

(1) **Regnault's Method.** Two similar glass globes, each provided with a stop cock and a hook, are employed. One of these is simply used as a counterpoise on the balance to avoid errors due to changes of atmospheric

temperature and pressure. The other globe (whose capacity has been found out beforehand by weighing it empty and then filled with distilled water at a known temperature) is evacuated by means of an air-pump and then weighed. Next, it is filled with the gas and weighed once again. From the results obtained the density of the gas is calculated as in the following example.

Example 1. *In a determination of the density of nitrogen by Regnault's method the following results were obtained :—*

Difference between the weights of the globes one of which was evacuated = 10·425 *gm.*

Difference between the weights of the globes when the evacuated globe was filled with nitrogen at 0°*C. (this globe being the heavier)* = 0·614 *gm.*

The capacity of the nitrogen globe = 8·676 *litres.*

Atmospheric pressure = 773 *mm.*

Find out the density of nitrogen relative to hydrogen and its molecular weight.

Weight of nitrogen in the globe = 10·425 + 0·614 or 11·039 gm.

Volume of the gas in the globe reduced to N.T.P.

$$= 8{\cdot}676 \times \frac{773}{760} \text{ litres.}$$

Weight of this volume of hydrogen

$$= 8{\cdot}676 \times \frac{773}{760} \times 0{\cdot}09 \text{ gm}$$

Vapour density of nitrogen

$$= 11{\cdot}039 \times \frac{1}{8{\cdot}676} \times \frac{760}{773} \times \frac{1}{0{\cdot}09} \text{ or } \mathbf{13{\cdot}9}$$

∴ Molecular weight of nitrogen = 13·9 × 2 or **27·8.**

(2) **Bunsen's Effusion Method.** The process of *effusion*, *i.e.* the forcing of a gas through a small aperture obeys Graham's law, which may be stated as follows :

The relative rates of effusion (and also of diffusion) of gases are inversely proportional to their densities. Or,

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

If t_1 and t_2 are the times of effusion of the two gases and d_1 and d_2 their respective densities, we have :

$$\frac{\mathbf{d_1}}{\mathbf{d_2}} = \frac{\mathbf{t_1^2}}{\mathbf{t_2^2}}$$

This last relation is very useful, for it may be directly employed for the calculation of densities of gases and their molecular weights.

Example 2. *Calculate the molecular weight of an unknown gas which under precisely similar conditions takes* 1·117 *times as long as oxygen to diffuse through an aperture.* (*Punjab B. Sc.*, 1924.)

The molecular weight of oxygen is 32. If the molecular weight of the unknown gas be M, we have :

$$\frac{M}{32} = \frac{(1{\cdot}117)^2}{1^2}; \text{ since } \frac{M_1}{M_2} = \frac{d_1}{d_2}$$

$$\therefore M = (1{\cdot}117)^2 \times 32 \text{ or } \mathbf{39{\cdot}9}.$$

8. Determination of Vapour Densities of Volatile Liquids and Solids. In the case of volatile liquids and solids the following methods of vapour density determination are employed, the first being the most frequently used :—

(1) **Victor Meyer's Air-displacement Method.** In this method a known weight of the substance is allowed to vaporize *very rapidly*. The vapour displaces its own volume of air which is collected over water and measured under the atmospheric conditions of temperature and pressure.

Example 3. *In a Victor Meyer determination of the vapour density,* 0·0926 *gm. of a liquid gave* 28·9 *c.c. of gas, collected over water and measured at* 16°C. *and* 753·5 *mm. pressure. Calculate the vapour density of the liquid.* (*Aq. tension at* 16° = 13·5). (*Inter. B. Sc., Manc.*)

Volume of dry air reduced to N.T.P.

$$= 28{\cdot}9 \times \frac{273}{289} \times \frac{753{\cdot}5 - 13{\cdot}5}{760} \text{ or } 26{\cdot}6 \text{ c.c.}$$

Weight of this volume of hydrogen
$= 26{\cdot}6 \times 0{\cdot}00009$ or $0{\cdot}002394$ gm.

Vapour density of the liquid $= \frac{0{\cdot}0926}{0{\cdot}002394}$ or **38·7**.

(2) **Dumas' Method.** In this method a glass bulb is weighed full of air and then full of the vapour under known conditions of temperature and pressure. Lastly, the capacity of the bulb is determined by weighing the bulb full of water. The following example illustrates the method of calculation.

Example 4. *The following results were obtained in a determination of the vapour density of camphor by Dumas' method :—*

Weight of the bulb full of air at 13°C. *and* 742 *mm.* $= 27{\cdot}400$ *gm.*

Weight of the bulb full of vapour at 244°C. *and* 742 *mm.* $= 27{\cdot}966$ *gm.*

Weight of the bulb full of water $= 263{\cdot}40$ *gm.*

Calculate the molecular weight of camphor.

The capacity of the bulb is nearly $263{\cdot}40 - 27{\cdot}40$ or $236{\cdot}0$ c.c.

The weight of air which fills the bulb at 13°C. and 742 mm. $= 236{\cdot}0 \times \frac{273}{286} \times \frac{742}{760} \times 0{\cdot}00009 \times 14{\cdot}4$ or $0{\cdot}285$ gm.

The weight of the vacuous bulb
$= 27{\cdot}400 - 0{\cdot}285$ or $27{\cdot}115$ gm.

∴ The weight of vapour in the bulb at 244°C. and 742 mm. $= 27{\cdot}966 - 27{\cdot}115$ or $0{\cdot}851$ gm.

Hence we see that $236{\cdot}0$ c.c. of vapour at 244°C. and 742 mm. or $236 \times \frac{273}{517} \times \frac{742}{760}$ c.c. of vapour at N.T.P., weigh $0{\cdot}851$ gm.

$\therefore$ 1 c.c. of the vapour at N.T.P. weighs

$$\frac{0{\cdot}851 \times 517 \times 760}{236 \times 273 \times 742} \text{ or } 0{\cdot}00699 \text{ gm.}$$

$\therefore$ The Vapour Density of camphor $= \frac{0{\cdot}00699}{0{\cdot}00009}$ or $77{\cdot}7$;

and its Molecular Weight $= 77{\cdot}7 \times 2$ or **155·4.**

(3) **Hofmann's Method.** This method is employed to determine the vapour densities of substances that decompose when vaporized under the ordinary pressure. The apparatus employed consists of a wide barometer tube which is graduated on one side from the top downwards in cubic centimetres, and on the other from the bottom upwards in millimetres. This is surrounded by a jacket through which is passed the vapour of a liquid boiling at a suitable temperature.

A small known quantity of the substance is introduced into the tube and allowed to vaporize in the *Torricellian vacuum* above the mercury column. When the vaporization is complete and the level of the mercury column becomes constant, the volume of the vapour and the depression of the mercury column are noted.

Example 5. *In a determination of the vapour density of heptane by Hofmann's method the following results were obtained :—*

The weight of substance taken $= 0{\cdot}0769$ *gm., the volume of the vapour* $= 69{\cdot}77$ *c.c., the temperature* $= 99{\cdot}6^{\circ}C.$; *barometric reading* $= 749{\cdot}0$ *mm.; the height of mercury column* $= 493{\cdot}4$ *mm.*

Find the vapour density of the substance.

The volume of the vapour at $99{\cdot}6^{\circ}$C. and under $749{\cdot}0 - 493{\cdot}4$ or $255{\cdot}6$ mm. pressure $= 69{\cdot}77$ c.c.

The volume of the vapour reduced to N.T.P.

$$= 69{\cdot}77 \times \frac{273}{372{\cdot}6} \times \frac{255{\cdot}6}{760} \text{ or } 17{\cdot}19 \text{ c.c.}$$

The weight of 1 c.c. of the vapour at N.T.P.

$$= \frac{0{\cdot}0769}{17{\cdot}19}$$

∴ The density of the vapour at N.T.P.

$$= \frac{0{\cdot}0769}{17{\cdot}19} \times \frac{1}{{\cdot}00009} \text{ or } \mathbf{49{\cdot}7}.$$

(4) **Lumsden's Method.** In this method a known weight of the substance is allowed to vaporize in a constant-volume air thermometer, and the pressure required to keep the volume constant is read from a manometer attached to the apparatus. From the increase in pressure due to the vapour of the substance, the molecular weight of the latter is calculated, as in the following example.

Example 6. 0·059 *gm. of ether was allowed to vaporize in a constant-volume air thermometer at* 100°C. *The volume of the bulb was* 50 c.c. *and the initial and final pressures indicated by the manometer were* 740 *and* 1110 *mm. respectively. Calculate the vapour density and the molecular weight of ether.*

Volume of vapour at N.T P.

$$= 50 \times \frac{273}{373} \times \frac{370}{760} \text{ or } 17{\cdot}8 \text{ c.c.}$$

Weight of this volume of hydrogen

$$= 17{\cdot}8 \times 0{\cdot}00009 \text{ or } 0{\cdot}00160 \text{ gm.}$$

$$\text{Vapour density of ether} = \frac{0{\cdot}059}{0{\cdot}00160} \text{ or } \mathbf{37}.$$

∴ Molecular weight of ether = 37 × 2 or **74**.

9. Direct Determination of Molecular Weights by Avogadro's Hypothesis. From Avogadro's hypothesis it follows that a *'gram-molecular weight'* (*i.e.* the molecular weight expressed in grams) of *any* gas occupies a constant volume. This volume is called *gram-molecular volume*, or *G.M.V.*, and its value at N.T.P. is found to be **22·4 litres.** Thus, 2 grams of hydrogen, 32 grams of oxygen, or 71 grams of chlorine will occupy 22·4 litres at N.T.P.

The fact that *a gram-molecular weight of any gas or vapour occupies a volume of* 22·4 *litres at N.T.P.* may be used for the direct calculation of molecular weights from experimental results.

Example 7. 0·333 *gm. of alcohol displaced in a victor Meyer apparatus* 171 *c.c. of air measured over water at* 15°C. *The barometric pressure was* 773 *mm. Calculate the molecular weight of alcohol.* (*Aq. tension at* 15°*C* = 13 *mm.*)

The volume of dry air reduced to N.T.P.

$$= 171 \times \frac{273}{288} \times \frac{773 - 13}{760} \text{ or } 162 \text{ c.c.}$$

This volume would be occupied by 0·333 gm. of alcohol vapour.

Hence, the weight of alcohol vapour that would occupy 22·4 litres at N.T.P., *i.e.* its *molecular weight*

$$= 0{\cdot}333 \times \frac{22{\cdot}4}{0{\cdot}162} \text{ or } \mathbf{46{\cdot}0.}$$

10. Gaseous Dissociation. When a gas dissociates on heating we have, for every temperature, a definite state of equilibrium between the simpler and the undissociated molecules. *The fraction of the whole which exists as simpler molecules is called the* **degree of dissociation** *of the substance at the given temperature.*

11. Calculation of the Degree of Dissociation from the Vapour Density. Let x be the degree of dissociation and n the number of simpler molecules into which one molecule of the dissociating substance splits up.

At equilibrium the number of simpler molecules present for every molecule of the undissociated substance initially present will be nx, and the number of undissociated molecules will be $1 - x$. Hence the total number of molecules will be $1 - x + nx$ or $1 + x\,(n - 1)$.

By Avogadro's Hypothesis—

$$\frac{\text{Volume after dissociation}}{\text{Volume before dissociation}} = \frac{1 + x(n - 1)}{1}$$

Or, since the densities are inversely proportional to the volumes,

$$\frac{\text{Density before dissociation}}{\text{Density after dissociation}} = \frac{1 + x(n - 1)}{1}$$

If the density before dissociation be represented by D and the density after dissociation, *i.e.*, the observed vapour density at the higher temperature, by d, we have—

$$\frac{D}{d} = 1 + x(n - 1)$$

$$\therefore \mathbf{x} = \frac{\mathbf{D - d}}{\mathbf{d(n - 1)}}$$

Example 8. *The vapour density of nitrogen peroxide at* 90° *C. is* 24·8. *Calculate the degree of dissociation into NO_2 molecules at this temperature.*

From the equation

$$N_2O_4 \rightleftharpoons 2NO_2$$

we see that one N_2O_4 molecule breaks up to give two simpler molecules.

If x is the degree of dissociation at 90°C., the number of simpler molecules at equilibrium will be $2x$, and the number of undissociated molecules will be $1 - x$. Thus, for every molecule of the undissociated substance initially present we get at equilibrium $2x + 1 - x$ or $x + 1$ molecules.

By Avogadro's Hypothesis—

$$\frac{\text{Volume after dissociation}}{\text{Volume before dissociation}} = \frac{x + 1}{1}$$

Or, since the densities are inversely proportional to volumes,

$$\frac{\text{Density of the undissociated gas}}{\text{Observed density at 90°C.}} = \frac{x + 1}{1}$$

$$\therefore x = \frac{46 - 24{\cdot}8}{24{\cdot}8} \text{ or } \mathbf{0{\cdot}855}.$$

Example 9. *The vapour density of nitrogen peroxide at* 60°*C. is* 30·2. *Calculate the percentage by weight of NO_2 molecules present.*

As in Example 1, the degree of dissociation

$$x = \frac{46 - 30{\cdot}2}{30{\cdot}2} \text{ or } 0{\cdot}523.$$

∴ Percentage by weight of NO_2 molecules

$$= 0{\cdot}523 \times 100 \text{ or } \mathbf{52{\cdot}3}.$$

Example 10. *When phosphorus pentachloride is heated it gasifies and dissociates into trichloride and chlorine. At* 182° *the density of the gas mixtnre is* 73·5 *and at* 230° *the density is* 62. *Find the degree of dissociation at* 182° *and* 230° ($P=31$; $Cl=35{\cdot}5$). (*Punjab B. Sc.* 1930.)

The theoretical vapour density D of phosphorus pentachloride when no dissociation has occured is one-half its molecular weight, *i.e.*

$$\frac{31+35{\cdot}5\times 5}{2} \text{ or } 104{\cdot}25.$$

The observed vapour density d at $182^\circ = 73{\cdot}5$.

From the equation

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

we see that the number of simpler molecules, n, into which a molecule of phosphorus pentachloride splits up = 2.

Substituting these values in the formula

$$x = \frac{D-d}{d(n-1)}$$

we get :

The degree of dissociation of PCl_5 at 182°

$$= \frac{104{\cdot}25-73{\cdot}5}{73{\cdot}5(2-1)}$$

$$= \frac{30{\cdot}75}{73{\cdot}5} \text{ or } \mathbf{0{\cdot}418}.$$

Similarly, the degree of dissociation at 230°

$$= \frac{104{\cdot}25-62}{62} \text{ or } \mathbf{0{\cdot}0681}.$$

Example 11. 4·98 *gm. of ammonium carbamate, on being completely vaporized at* 200°C *was found to occupy* 7·60 *litres under a pressure of* 740 *mm. Calculate the degree of dissociation at* 200°C *according to the equation,*

$$OC{<}^{NH_2}_{ONH_4} \rightleftharpoons 2NH_3 + CO_2.$$

The calculation involves two steps :—

(*i*) *Calculate the vapour density of ammonium carbamate at* 200°*C*.

Volume of the vapour reduced to N.T.P.

$$= 7{\cdot}60 \times \frac{273}{473} \times \frac{740}{760} \text{ or } 4{\cdot}27 \text{ litres.}$$

Weight of 4·27 litres of hydrogen at N.T.P.

$$= 4{\cdot}27 \times 0{\cdot}09 \text{ or } 0{\cdot}384 \text{ gm.}$$

∴ Vapour density of ammonium carbamate at 200°C

$$= \frac{4{\cdot}98}{0{\cdot}384} \text{ or } 13{\cdot}0.$$

(*ii*) *Calculate the degree of dissociation* x.

The theoretical vapour density D of ammonium carbamate when no dissociation has taken place is one-half its molecular weight, *i.e.* 78/2 or 39.

The observed vapour density d at 200°C = 13.0.

The number of simpler molecules, n, into which a molecule of ammonium carbamate splits up = 3.

Substituting these values in the formula

$$x = \frac{D - d}{d(n - 1)}$$

we get :

$$x = \frac{39{\cdot}0 - 13{\cdot}0}{13{\cdot}0 \times 2} \text{ or } \mathbf{1{\cdot}00}.$$

Hence, we see that ammonium carbamate is *completely* dissociated at 200°C.

12. Kinetic Theory of Gases. From the kinetic theory of gases the following relation can be readily derived :

$$\mathbf{PV = \tfrac{1}{3}\, nmc^2}$$

where P is the pressure of the gas, V its volume, n the number of molecules present, m the mass of a single molecule, and c the **root mean square velocity** (R.M.S.V.).

According to Clark Maxwell the **average velocity** of the molecule of a gas is given by the relation :

Average velocity = R.M.S.V. × 0·9213.

While calculating the R.M.S. velocity and the average velocity all the quantities must be expressed in units of the *same* system, preferably the C.G.S. system, the pressure being expressed in dynes per square centimetre. This is obtained by multiplying the height of the mercury column in centimetres by the sp. gr. of mercury, *i.e.* 13·6, and the force of gravity, *i.e.* 981.

Example 12. *Find the average velocity of oxygen molecules at* 15°C *and* 770 *mm. pressure.*

Let us consider a gram molecule, *i.e.* 32 gm., of oxygen.

Its volume at N.T.P. is 22400 c.c.

Its volume at 15°C and 770 mm. pressure

$$= 22400 \times \frac{288}{273} \times \frac{760}{770} \text{ c.c.}$$

Its pressure in dynes per sq. cm. $= 77 \times 13{\cdot}6 \times 981$.

From the kinetic theory of gases we have :

$$PV = \tfrac{1}{3}\, nmc^2$$

Substituting the values of P, V, and nm, *i.e.* the total mass of 1 gm. molecule of oxygen, in the above equation we get c, *i.e.* the R.M.S. velocity of oxygen molecules at 15°C and 770 mm. pressure :

$$c = \sqrt{\frac{3PV}{nm}}$$

$$= \sqrt{\frac{3 \times 77 \times 13{\cdot}6 \times 981 \times 22400 \times 288 \times 760}{273 \times 770 \times 32}} \text{ cm. per sec.}$$

$$= 47148 \text{ cm. per sec.}$$

∴ Average velocity of oxygen molecules at 15°C and 770 mm. pressure

$$= 47148 \times 0{\cdot}9213 \text{ or } 43440 \text{ cm. per sec.}$$

Note. It should be observed that the actual pressure of the gas, 77 cm., caucels out in the final fraction. The

velocity of the molecules of a gas is, therefore, independent of the pressure, but not of temperature.

13. Specific Heats of Gases. The heat required to raise the temperature of 1 gram of a gas from 0° to 1°C, the volume being kept unchanged, is called the *specific heat of the gas at constant volume*, and is generally denoted by *Cv*. The heating of the gas without allowing it to expand, of course, results in an increase of pressure. If the gas benow allowed to expand until the pressure falls to its original volume, the gas will be cooled. To keep its temperature at 1°C more heat must, therefore, be added. The total heat supplied to 1 gram of a gas to raise its temperature from 0° to 1°C so that the pressure remains unaltered is called the *specific heat of the gas at constant pressure*, and is denoted by *Cp*.

The ratio *Cp*/*Cv* is usually denoted by γ, and can be shown theoretically to possess the value :

$$\gamma = \frac{5 + E}{3 + E}$$

where E stands for the energy absorbed by the molecule, for performing *intra*-molecular work, *i.e.* increasing the speed of rotation of atoms within the molecule. In the case of *mon*atomic gases the value of *E* is evidently zero and hence we have :

$$\gamma = 5/3 \text{ or } \mathbf{1{\cdot}67}.$$

For di- and tri- atomic gases the typical values of γ are respectively **1·41** and **1·33**.

There are two methods in use for practically determining the value of γ :

(1) **Kundt's Method.** In this method the velocity of sound (V) in the given gas is determined, and the value of γ is calculated from the relation

$$\gamma = \frac{\mathbf{V^2 D}}{\mathbf{P}}$$

where P is the pressure of the gas and D its density.

Note. The values of *P* and *D* must be expressed in units of the *same* system, preferably the C.G.S. system, the pressure being expressed in *dynes per square centimetre*.

Example 13. *The velocity of sound in argon at N.T.P. is* 1000 *feet per second. Calculate the ratio Cp/Cv of the gas and its atomicity.* (*V. D. of argon* = 19·97).

Velocity of sound in argon at N.T.P.

$= 1000 \times 12 \times 2{\cdot}54$ or 30480 cm. per sec.

Pressure of the gas $= 76 \times 13{\cdot}6 \times 981$ dynes per eq. cm.

Density of the gas $= 19{\cdot}97 \times 0{\cdot}00009$ or $0{\cdot}001797$ gm. per c.c.

Substituting these values in the formula

$$\frac{Cp}{Cv} = \frac{V^2 D}{P}$$

we have :

$$\frac{Cp}{Cv} = \frac{30480 \times 30480 \times 0{\cdot}001797}{76 \times 13{\cdot}6 \times 981} \text{ or } \mathbf{1{\cdot}65}.$$

Hence, the atomicity of argon is **1**.

(2) **Clement and Desorme's Method.** Here a quantity of compressed (or rarefied) gas (at P_1), contained in a carboy connected to a manometer, is put into communication with the atmosphere for one or two seconds (not more), so that its pressure may fall (or rise) adiabatically to that of the atmosphere (P). The gas is now again shut off from the atmosphere, and allowed to attain its original temperature, when the rise (or fall) of pressure is noted If P_2 represents the final pressure, we have :

$$\gamma = \frac{\log P_1 - \log P}{\log P_1 - \log P_2}$$

Example 14. *A quantity of gas at an initial pressure of* 771·6 *mm. is allowed to expand adiabatically to atmospheric pressure* (760·0 *mm.*). *When the gas has regained its original temperature, the pressure was found to be* 763·6 *mm. Calculate the ratio of the specific heats of the gas and its atomicity.*

The ratio of the specific heats of the gas is given by the expression

$$\gamma = \frac{\log 771{\cdot}6 - \log 760{\cdot}0}{\log 771{\cdot}6 - \log 763{\cdot}6}$$

$$= \frac{2{\cdot}8874 - 2{\cdot}8808}{2{\cdot}8874 - 2{\cdot}8828}$$

$$= \mathbf{1{\cdot}43}.$$

$\therefore$ Atomicity of the gas is **2**.

EXERCISES

1. The speeds of diffusion of CO_2 and of ozone were found by Soret to be as 0·29 is to 0·271. The relative density of CO_2 is 22 when H = 1. What is the relative density of ozone ? (*Punjab B. Sc.* 1929.)

2. A gas was allowed to diffuse into air through a porous diaphragm. The pressure on both sides of the diaphragm was equal throughout the experiment. The volume of air which entered was 15 c.c. and the volume of gas which escaped was 15·21 c.c. What was the density of the gas in question compared with that of air ?

3. A liquid weighing 0·2457 gm. displaced, in Meyer's apparatus, 30·0 c.c. of air measured over water at 17°C when the barometer stood at 774·5 mm. What is the vapour density of the substance ? (Aqueous tension at 17° = 14·4 mm.) (*1st Year Hons., Manc.*)

4. Calculate the molecular weight of chloroform from the following data obtained by Dumas' method :—

Capacity of the bulb = 127·0 c.c., temperature of the bath = 136·0°C ; weight of vapour = 0·4524 gm.

5. In a determination of vapour density by Victor Meyer's method 0·406 gm. of a certain substance expelled 170 c.c. of air, measured over water at 15·1°C and 763 mm. pressure. Find the molecular weight of the substance. (*Punjab B. Sc. Agr.* 1924.)

6. In a determination of the molecular weight of a substance by the Victor Meyer method, 0·1680 gm. of the substance gave 49·4 c.c. of vapour at 20°C and 740 mm. pressure. Calculate the molecular weight of the substance. (*Punjab, B. Sc. Agr.*, 1926.)

7. In a determination of the vapour density of a substance by Dumas' method the following results were obtained :—

Wt. of empty bulb in air	... 25·723 gm.
,, bulb + vapour (16°C)	... 25·935 ,,
Temperature of sealing of bulb	... 105°C.
Capacity of globe by weighing of water	... 172 c.c.
Wt. of 1 c.c. of hydrogen at N.T.P. is	0·00009gm.
,, ,, air ,,	0·00129 ,,

Calculate the vapour density of the substance.
(*Punjab. B. Sc., Agr.*, 1927.)

8. The vapour density of nickel carbonyl at 100°C is 70·8. Calculate the degree of dissociation, at this temperature, according to the equation

$$Ni(CO)_4 \rightleftharpoons Ni + 4CO.$$

9. At 49·7° and under a pressure of 182 mm. of mercury the density of nitrogen peroxide was 1·89 whilst that of the undissociated peroxide was 3·18 (air = 1). Calculate the degree of dissociation. At what pressure would the mixture be half dissociated ? (*London B. Sc.*)

10. At 182° and 760 mm. pressure the vapour density of phosphorus pentachloride is 73·5. Calculate the degree of dissociation of the substance, and also the partial pressures and concentrations in moles per litre of PCl_5, PCl_3, and Cl_2, when a gram-molecule of PCl_5 is heated at 760 mm. to 182°C.

11. Victor Meyer found the vapour density of iodine to be 81·5 at 1250°. Calculate the percentage dissociation at this temperature according to the equation.

$$I_2 \rightleftharpoons 2I.$$

12. Ammonium carbamate, on being vaporized, dissociates completely, according to the equation

$$NH_2.CO.ONH_4 \rightleftharpoons 2NH_3 + CO_2.$$

What will be the volume occupied if 4·00 gm. of the substance be vaporized at 110°C and 755 mm. pressure ?

13. The velocity of sound in hydrogen at N.T.P. is 1255 metres per sec. What is the ratio of the specific heats of the gas and its atomicity ?

14. The mean distance between two nodes for a tube filled with dry CO_2 was found to be 4·528 cm., when filled with dry air under the same conditions the distance was found to be 5·948 cm. If the ratio Cp/Cv for air is 1·41 and its density is 14·45, calculate the ratio Cp/Cv for CO_2.
(*B. Sc. Hons. Manc.*)

15. A certain quantity of a gas at an initial pressure of 772·9 mm. is allowed to expand adiabatically to the atmospheric pressure. When the gas regained its original temperature, the pressure was found to be 763·8 mm. The barometer stood at 759·9 mm. Calculate the ratio Cp/Cv of the gas and its atomicity.

16. Find the R.M.S. velocity and the average velocity of CO_2 molecules at 18°C. and 80 cm. pressure.

Answers

1. 25. **2.** 0·9725. **3.** 96·7. **4.** 118·5.
5. 55·8. **6.** 83·2. **7.** 37·7. **8.** 0·0666.
9. 0·683 ; 477 mm.
10. 0·418 ; Partial pressures : $PCl_5 = 0·410$ atmos., PCl_3 and $Cl_2 = 0·295$ atmos ;
Concentrations : $PCl_5 = 0·01098$; PCl_3 and $Cl_2 = 0·007903$.
11. 56%. **12.** 4·87 litre. **13.** 1·4 ; 2. **14.** 1·24.
15. 1·42 ; 2. **16.** 40600 cm. per sec.; 37405 cm. per sec.

CHAPTER III

DETERMINATION OF MOLECULAR WEIGHTS IN SOLUTION

14. Determination of Molecular Weights from Osmotic Pressure. Van't Hoff established a complete analogy between the gaseous state and the state of a substance in dilute solution. The ordinary gas laws are obeyed by dilute solutions just as well as by gases. The gas equation

$$PV=RT$$

is also the equation which connects the pressure (*i.e.* osmotic pressure), volume, and temperature of a dilute solution. The value of the constant R has been shown to be the same both for solutions and gases. This analogy between the two states has been utilized for determining the molecular weights of substances in solution.

It has been found that a gram molecule of any gas occupies a volume of 22·4 litres at 0°C and 760 mm. pressure. It follows, therefore, that if we have a solution of a substance containing 1 gram molecule dissolved in 22·4 litres, it will exert, at 0°C, an osmotic pressure of 760 mm. For other temperatures and concentrations the osmotic pressure can be calculated with the help of the gas laws, if the molar concentration of the solution is known. Conversely, if we know the osmotic pressure, the concentration, and the temperature of the solution of a substance, we can readily calculate the molecular weight of the dissolved substance.

Example 1. *Calculate the osmotic pressure at* 25°C *of a* 5 *per cent solution of urea.* (*Punjab B. Sc.* 1923.)

A gram molecule of urea, $CO(NH_2)_2$, *i.e.* 60 gm., when present in 22·4 litres of a solution at 0°C, exerts an osmotic pressure of 1 atmosphere.

5 gm. of urea present in 22·4 litres of a solution at 0°C would, therefore, exert an osmotic pressure of $1 \times \frac{5}{60}$ atmosphere.

Hence, 5 gm. of urea, when present in 100 c.c. of a solution at 25°C, would exert an osmotic pressure of

$$1 \times \frac{5}{60} \times \frac{22{\cdot}4 \times 1000}{100} \times \frac{298}{273} \text{ atmos.}$$

$$= \mathbf{20{\cdot}4 \text{ atmos.}}$$

Example 2. 7·20 *gm. of a substance dissolved in* 100 *gm. of water gave rise to an osmotic pressure of* 9·65 *atmospheres at* 22°C. *Calculate the molecular weight of the substance.* (*Punjab B. Sc.* 1926,27.)

Volume of 100 gm. of water and hence that of the solution is approximately 100 c.c.

At N.T.P. this volume would become

$$100 \times \frac{273}{295} \times \frac{9{\cdot}65}{1} \text{ or } 893 \text{ c.c.}$$

Weight of the substance present in 893 c.c. of the solution at 0°C and an osmotic pressure of 1 atmos. = 7·6 gm.

Hence the weight of the substance present in a G.M.V. or 22·4 litres of the solution at 0°C and an osmotic pressure of 1 atmos.

$$= 7{\cdot}6 \times \frac{22{\cdot}4}{0{\cdot}893} \text{ or } 180.$$

∴ Molecular weight of the substance is **180.**

Example 3. *Calculate the concentration of a solution of urea that is isotonic with a solution containing* 10 *grams of cane sugar per litre.*

We know that equi-molar solutions are *isotonic*, *i.e.* they exert the same osmotic pressure at the same temperature.

A solution containing 10 gm. of cane sugar per litre is $\frac{10}{342}$ molar (since $C_{12}H_{22}O_{11}=342$). This will be isotonic with a $\frac{10}{342}$ molar solution of urea ($NH_2.CO.NH_2=60$).

Hence, the concentration of urea solution

$$=\frac{10}{342}\times 60 \text{ or } \mathbf{1{\cdot}76 \text{ gm. per litre.}}$$

Example 4. *Pfeffer found the osmotic pressure of a 1 per cent solution of cane sugar at 0° to be 49·3 cm. of mercury. Calculate from this the value of the solution constant, R.*

Osmotic pressure of the solution in grams per square centimetre $=49{\cdot}3\times 13{\cdot}6$. (Absolute density of mercury = 13·6 gm./c.c.)

Volume of solution that contains 1 gram-molecule of cane sugar ($C_{12}H_{22}O_{11}=342$)

$$=100\times 342 \text{ or } 34200 \text{ c.c.}$$

Temperature $=273°$ Absolute.

Substituting these values in the gas equation, $PV=RT$, we have :

$$R=\frac{49{\cdot}3\times 13{\cdot}6\times 34200}{273}$$

$$=\mathbf{84000} \text{ (in gram·cm. units).}$$

15. Determination of the Degree of Dissociation. The degree of dissociation in solution can be determined in exactly the same manner as that in the gaseous state (p. 39). Let x be the degree of dissociation and n the number of ions into which one molecule of the electrolyte splits up. We shall then have in solution $1-x$ undissociated molecules and nx ions, *i.e.* $1+x(n-1)$ particles in all.

Let P be observed osmotic pressure and p the theoretical osmotic pressure calculated by neglecting dissociation.

Since the osmotic pressure is always proportional to the number of particles present, we have :

$$\frac{P}{p} = \frac{1 + x(n-1)}{1}$$

$$\therefore \quad \mathbf{x = \frac{P - p}{p(n-1)}}$$

Example 5. *A solution of urea containing* 4·00 *gm. in* 100 *c.c. was found to be isotonic with a* 4·50 *per cent solution of magnesium chloride. Calculate (a) the degree of dissociation of magnesium chloride in the solution, and (b) its apparant molecular weight.*

(*a*) CALCULATION OF THE DEGREE OF DISSOCIATION :

The osmotic pressure of a solution of urea ($NH_2.CO.NH_2 = 60$) containing 60 gm. in 22·4 litres = 1 atmos.

Hence the osmotic pressure of the urea solution containing 4·00 gm. in 100 c.c., and therefore that of 4·50 per cent solution of magnesium chloride

$$= 1 \times \frac{4{\cdot}00}{0{\cdot}1} \times \frac{22{\cdot}4}{60} \text{ or } 14{\cdot}9 \text{ atmos.}$$

Theoretical osmotic pressure of 4·50 per cent magnesium chloride ($MgCl_2 = 95$) solution, assuming no dissociation to have occurred

$$= 1 \times \frac{4{\cdot}50}{0{\cdot}1} \times \frac{22{\cdot}4}{95} \text{ or } 10{\cdot}6 \text{ atmos.}$$

Substituting these values in the formula

$$x = \frac{P - p}{p(n-1)}$$

where x represents the degree of dissociation of the electrolyte, n the number of ions into which a molecule of the electrolyte breaks up (*i.e.* 3 in this case), P the observed osmotic pressure, and p the theoretical osmotic pressure assuming no dissociation to have occurred, we have

$$x = \frac{14{\cdot}9 - 10{\cdot}6}{10{\cdot}6 \times (3-1)} = 0{\cdot}203, \text{ or } \mathbf{20{\cdot}3}\,\%.$$

(*b*) CALCULATION OF THE APPARENT MOLECULAR WEIGHT.

The solution of urea (molecular weight = 60) containing 4·00 gm. per 100 c.c. is isotonic with the magnesium chloride solution containing 4·50 gm. per 100 c.c. Hence, if *M* represents the apparent molecular weight of magnesium chloride in the solution, we have :

$$\frac{4{\cdot}00}{60} = \frac{4{\cdot}50}{M}$$

$$\therefore M = \frac{4{\cdot}50 \times 60}{4{\cdot}0} = 67{\cdot}5.$$

16. Determination of Molecular Weights from Lowering of Vapour Pressure. By a thermodynamical method Van't Hoff established the following relation between the osmotic pressure and the "**relative lowering**" of the vapour pressure, *i.e.* the ratio of the observed lowering of the vapour pressure to the vapour pressure of the pure solvent :

$$\frac{p_1 - p_2}{p_1} = P.\frac{M}{sRT} \qquad \ldots \qquad \ldots (1)$$

where p_1 and p_2 represent the vapour pressure of the solvent and the solution respectively, $\frac{p_1 - p_2}{p_1}$ the "relative lowering" of the vapour pressure, P the osmotic pressure of the solution, M the molecular weight of the solvent in the *gaseous state*, s the absolute density of the solvent (or practically that of the solution, if dilute), and T the temperature of the solution on the absolute scale. Since, for any solvent at a given temperature, the expression M/sRT is constant, *the lowering of vapour pressure is proportional to the osmotic pressure P.*

We can eliminate P in equation (1) by the use of the general equation

$$PV = nRT$$

where V represents the volume of the solution, and n the number of mols. of the solute. If N is the number of mols. of solvent, we have

$$V = \frac{MN}{s}$$

Putting $\frac{MN}{s}$ for V in the general equation given above we get

$$P = nRT \cdot \frac{s}{MN}$$

Substituting this value of P in equation (1) we get* :—

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N} \quad \ldots \quad \ldots (2)$$

This last relation can be used for the determination of the molecular weights of dissolved substances. Let W be the weight of the solvent in the solution and M its molecular weight in the *gaseous state*, and w the weight of the solute and m its molecular weight, then

$$\frac{n}{N} = \frac{\frac{w}{m}}{\frac{W}{M}} = \frac{wM}{mW}$$

By substituting wM/mW for n/N in equation (2) we get the relation

$$\frac{p_1 - p_2}{p_1} = \frac{wM}{mW} \quad \ldots \quad \ldots (3)$$

which can be directly used for determining the molecular weight of a dissolved substance when the relative lowering produced by a given amount of the solute in a given weight of the solvent is known.

A simple method for determining experimentally the relative lowering of vapour pressure is as follows :—

A slow current of dry air is drawn in succession through

(*i*) a series of three or four "potash bulbs" containing the solution (vapour pressure p_2),

(*ii*) a similar series of bulbs containing the solvent (vapour pressure p_1), and

(*iii*) a series of bulbs containing sulphuric acid or some other suitable absorbent for the solvent.

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*The relation deduced here is approximate and holds good for dilute solutions.

In the first series of bulbs the air becomes saturated up to p_2 with the vapour of the solvent. In the second series of bulbs it is further saturated to p_1. The loss of weight in the first and the second series of bulbs is proportional to p_2 and $p_1 - p_2$ respectively.

Example 6. *Van't Hoff showed that the relation* $\frac{p_1 - p_2}{p_1} = \frac{n}{N}$ *holds good for dilute solutions, where* p_1 *and* p_2 *represent the vapour pressures of the solvent and the solution respectively, and* n *and* N *represent the number of molecules of the solute and the solvent respectively.*

A current of dried air was drawn through a solution of 3·500 *grams of a substance in* 100 *grams of ethyl alcohol, and then passed through ethyl alcohol alone. The loss of weight of the former liquid was* 0·8759 *gram and of the alcohol* 0·0241 *gram. Using the relation given above, calculate the molecular weight of the dissolved substance.* (*Punjab B. Sc.* 1924.)

The loss of weight of the solution (*i.e.* 0·8759 gm.) and that of the pure solvent (*i.e.* 0·0241 gm.) are respectively proportional to p_2 and $p_1 - p_2$, the total loss (*i.e.* 0·8759 + 0·0241 = 0·9000 gm.) being proportional to p_1.

The ratio n/N of the molecules of the solute and the solvent will be the same as the ratio of their quantities, expressed in gram-molecules, present in the solution, *i.e.*

$$\frac{\frac{3{\cdot}500}{m}}{\frac{100}{46}} \text{ or } \frac{3{\cdot}500 \times 46}{100m}$$

where m represents the molecular weight of the dissolved substance, 46 being the molecular weight of ethyl alcohol, C_2H_5OH, as determined by the vapour density method.

Substituting the above values in Van't Hoff's equation

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N}$$

we get

$$\frac{0{\cdot}0241}{0{\cdot}9000} = \frac{3{\cdot}500 \times 46}{100m}$$

$$\therefore \qquad m = \frac{3{\cdot}500 \times 46}{100} \times \frac{0{\cdot}9000}{0{\cdot}0241} = \mathbf{60{\cdot}1.}$$

Example 7. *The vapour pressure of water at* 20°*C is* 17 *mm. Calculate the vapour pressure of a solution of* 3·0 *gm. of urea in* 50 *gm. of water.*

According to Van't Hoff the following relation holds good for dilute solutions:

$$\frac{p_1 - p_2}{p_1} = \frac{wM}{mW}$$

where p_1 and p_2 represent the vapour pressures of the solvent and the solution reepectively, w and W are the respective quantities of the solute and the solvent in the solution, while m and M are their respective molecular weights.

In the present case we have :

$$p_1 = 17 \text{ mm.}$$
$$w = 3{\cdot}0 \text{ gm.}$$
$$W = 50 \text{ gm.}$$
$$m = 60$$
$$M = 18.$$

Substituting these values in the above equation we get :

$$\frac{17 - p_2}{17} = \frac{3{\cdot}0 \times 18}{60 \times 50}$$

whence $$p_2 = \mathbf{16{\cdot}69 \text{ mm.}}$$

17. Association in Solution. In some organic solvents the molecules of certain substances undergo polymerization or association. The condition of the solute molecules in such cases can be ascertained by finding the molecular weight in solution as well as in the gaseous state.

Example 8. *A current of dry air was passed in succession through two sets of bulbs containing respectively a solution of* 3·2 *gm. of a substance in* 50 *gm. of benzene, and pure benzene. The loss in weight sustained by the*

solution was 0·6632 *gm. and by benzene* 0·0288 *gm. The vapour density of the substance (solute) was* 30. *Determine the molecular condition of the substance in benzene solution.*

Loss in weight of solution = 0·6632 gm.
,, ,, benzene = 0·0288 ,,
∴ Total loss in weight = 0·6920 ,,

If p_1 represents the vapour-pressure of pure benzene and p_2 that of the solution, the loss in weight sustained by the solution will be proportional to p_2 and that by the solvent to $p_1 - p_2$, the sum of the two being proportional to p_1.

The ratio n/N of the molecules of the solute and the solvent will be the same as the ratio of their quantities, expressed in gram-molecules, present in the solution, *i.e.*

$$\frac{\frac{3{\cdot}2}{m}}{\frac{50}{78}} \text{ or } \frac{3{\cdot}2 \times 78}{50m}$$

where m represents the molecular weight of the dissolved substance while 78 is the molecular weight of benzene, C_6H_6, in the gaseous state.

Substituting the above values in the equation

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N}$$

we get

$$\frac{0{\cdot}0288}{0{\cdot}6920} = \frac{3{\cdot}2 \times 78}{50m}$$

$$\therefore m = \frac{3{\cdot}2 \times 78}{50} \times \frac{0{\cdot}6920}{0{\cdot}0288} = 120.$$

Now, the vapour density of the substance = 30.

∴ Molecular weight of the substance in the gaseous state = 30 × 2 = 60.

Hence, we see that in benzene solution the substance forms molecular complexes consisting of two molecules each.

18. Determination of Molecular Weights by Steam Distillation. The vapour pressure of a liquid at a given temperature is unaffected by the presence of another liquid that is non-miscible with it. A mixture of two immiscible liquids will therefore distil when the sum of their vapour pressures p_1 and p_2 is equal to the atmospheric pressure P, *i.e.*

$$P = p_1 + p_2.$$

This fact forms the basis of steam-distillation and is employed for the determination of molecular weights of liquids which are not miscible with water.

The relative quantities of water and the liquid that is steam-distilled, w_1 and w_2, which pass over are proportional to *(i)* their relative partial pressures at the temperature of distillation, p_1 and p_2, and *(ii)* their relative vapour densities or molecular weights. Now, the molecular weight of water is 18. If M is the molecular weight of the substance that is being steam-distilled, we have

$$\frac{w_1}{w_2} = \frac{p_1 \times 18}{p_2 \times M}$$

$$\therefore M = \frac{18 p_1 w_2}{p_2 w_1}$$

P, the atmospheric pressure, and the temperature of distillation are noted, p_1 is found by reference to the aqueous tension table, while p_2 is got from the relation

$$p_2 = P - p_1.$$

Example 9. *A carefully regulated current of steam was led into a heated mixture of nitrobenzene and water, and the temperature of distillation was found to remain constant at 98·0°C. The barometer stood at 760 mm. The volumes of water and nitrobenzene that distilled over during this time were found to be 100 c.c. and 42 c.c. respectively. The aqueous tension at 98·0°C is 707 mm. The specific gravity of nitrobenzene is 1·22, calculate its molecular weight.*

When a liquid is steam-distilled, the following relation holds good

$$\frac{w_1}{w_2} = \frac{p_1 \times 18}{p_2 \times M}$$

where w_1 and w_2 represent the relative weights of water and the liquid that pass over, p_1 and p_2 their respective vapour pressures at the temperature of distillation, and M the molecular weight of the liquid, 18 being the molecular weight of water.

In the present case we have :

$w_1 = 100$ gm.

$w_2 = 42 \times 1{\cdot}22$ gm. $= 51$ gm.

$p_1 = 707$ mm.

$p_2 = 760 - 707$ mm. $= 53$ mm.

Substituting these values in the above equation we get the molecular weight of nitrobenzene

$$M = \frac{707 \times 18 \times 51}{53 \times 100} = \mathbf{123.}$$

Example 10. *A liquid of molecular weight* 120 *has a partial pressure of* 20 *mm. while that of water-vapour is* 740 *mm. Calculate the weight of the former liquid which will be carried over by* 100 *grams of water-vapour.*

In this case we have :

$w_1 = 100$ gm.

$p_1 = 740$ mm.

$p_2 = 20$ mm.

$M = 120$

Substituting these values in the equation

$$\frac{w_1}{w_2} = \frac{p_1 \times 18}{p_2 \times M}$$

we get

$$\frac{100}{w_2} = \frac{740 \times 18}{20 \times 120}$$

Hence w_2, the weight of the liquid which will be carried over by 100 grams of water vapour,

$$= \frac{20 \times 120 \times 100}{740 \times 18} \text{ gm.} = \mathbf{18 \text{ gm.}}$$

19. Determination of Molecular Weights from the Elevation of Boiling-point. Since a liquid boils at a temperature at which its vapour pressure equals the atmospheric pressure, it follows that a solution, whose vapour pressure is always lower than that of the pure solvent must boil at a higher temperature than the pure solvent The elevation, E, of the boiling-point is proportional to the relative lowering of the vapour pressure, *i.e.*

$$E \propto \frac{p_1 - p_2}{p_1}$$

But

$$\frac{p_1 - p_2}{p_1} = \frac{w\mathrm{M}}{m\mathrm{W}}$$ [Art. 16.

which means that the relative lowering of vapour pressure of a solution will remain unaltered so long as the number of mols. of the solute, w/m, and the quantity of the solvent, W, and its molecular weight, M, are the same. This in other words means that equimolecular solutions of the same solvent will produce the same lowering of the vapour-pressure. But since the relative lowering of vapour-pressure is proportional to the elevation of boiling-point, we conclude that *the equimolecular quantities of different solutes dissolved in a given quantity of the same solvent produce the same elevation of the boiling-point.*

The elevation of the boiling-point produced by dissolving a gram molecule of any non-electrolyte in 100 grams of a given solvent is termed the **molecular elevation** of the solvent, and is denoted by K. Now, since the elevation of the boiling point is proportional to the quantity of the solute present, if we determine experimentally the elevation, $\triangle$, produced by s grams of the solute dissolved in

100 grams of the solvent, we can readily calculate the molecular weight, M, of the solute from the relation

$$\frac{M}{s} = \frac{K}{\triangle}$$

The above equation can also be used for calculating the value of k, s, or $\triangle$, if the values of the remaining three are known.

The values of the molecular elevation constant were originally obtained experimentally, using substances of known molecular weight. They can also be calculated theoretically from the relation

$$K = \frac{RT^2}{100L}$$

where T is the boiling point of the solvent on the *absolute scale*, and L is the latent heat of vaporization of the solvent. R is the gas constant in calories, its value being 1·985 calories, or approximately 2 calories. Table 1 gives the experimental values of K and also of K'. The latter represents the elevation of boiling point produced by dissolving 1 gram-molecule of a solute in 100 c.c. of the solvent. In the last column of the table are given the values of K calculated from the latent heat of vaporization.

TABLE 1.

MOLECULAR ELEVATION OF THE BOILING-POINT.

Solvent	K	K'	$K = \frac{RT^2}{100L}$
Water	5·2°C	5·4°C	5·15°
Ethyl alcohol	11·5	15·6	11·9
Ether	21·1	30·3	20·9
Benzene	25·7	31·5	26·1
Chloroform	38·8	27·7	38·0
Acetone	17·2	22·2	17·2

Example 11. *2·012 gm. of resorcinol are dissolved in* 100 *gm. of ether. The rise in the boiling-point is* 0·399°. *Find the molecular weight of resorcinol, being given that the boiling point of ether is* 34·8° *and the latent heat of vaporization* 84·5 *calories.* (*Inst. Chem. Phys.*, 1910.)

Boiling-point of ether on tne absolute scale

$$= 273 + 34{\cdot}8 = 307{\cdot}8^\circ$$

Latent heat of vaporization, $L = 84{\cdot}5$ cal.

$$R = 1{\cdot}985 \text{ cal.}$$

Substituting these values in the formula

$$K = \frac{RT^2}{100L}$$

we get

$$K = \frac{1{\cdot}985 \times (307{\cdot}8)^2}{100 \times 84{\cdot}5} = 22{\cdot}25.$$

Quantity of resorcinol, s, dissolved in 100 gm. of ether $= 2{\cdot}012$ gm.

Rise in the boiling-point, $\triangle$, caused by s gm. of the solute dissolved in 100 gm. of ether $= 0{\cdot}399^\circ$.

If M is the molecular weight of resorcinol, we have

$$\frac{M}{s} = \frac{K}{\triangle}$$

Substituting the values of s, K, and $\triangle$ in this equation we get

$$M = \frac{22{\cdot}25 \times 2{\cdot}012}{0{\cdot}399} = 112.$$

Example 12. *The boiling-point constant for water is* 5·2°*C. A normal solution of a monobasic acid was found to give an elevation of* 0·91°*C. Calculate the degree of dissociation of the acid.* (*Trinity Group, Cambridge.*)

Normal solution of a monobasic acid contains a mol. of the acid in 1000 c.c. or practically 1000 gm. of water.

Theoretical elevation of the boiling-point in the case of this solution, assuming no dissociation to have occurred,

$$= \frac{5{\cdot}2 \times 100}{1000} = 0{\cdot}52^{\circ}\text{C}.$$

Observed elevation $= 0{\cdot}91^{\circ}$C.

Substituting these values in the formula (see Art. 15)

$$x = \frac{\triangle - \delta}{\delta(n-1)}$$

where x represents the degree of dissociation, n the number of ions into which a molecule of the electrolyte breaks up (*i.e.* 2 in this case, since the acid is monobasic), $\triangle$ the observed elevation, and δ the theoretical elevation, assuming no dissociation to have occurred, we get

$$x = \frac{0{\cdot}91 - 0{\cdot}52}{0{\cdot}52 \times (2-1)} = \mathbf{0{\cdot}75}.$$

20. Determination of Molecular Weights from the Depression of Freezing-Point. Like the elevation of the boiling-point, the depression of the freezing-point is proportional to the relative lowering of vapour-pressure, and, as in the case of the elevation of boiling point, it can be shown that *the equimolecular solutions of different solutes dissolved in the same solvent produce the same depression of the freezing point.*

The depression of the freezing-point produced by dissolving a gram-molecule of any non-electrolyte in 100 grams of a given solvent is termed the **molecular-depression** of the solvent, and is denoted by K. Now, since the depression of the freezing-point is proportional to the quantity of the solute present, if we determine experimentally the depression, $\triangle$, produced by s grams of the solute dissolved in 100 grams of the solvent, we can readily calculate the molecular weight, M, of the solution from the relation

$$\frac{\mathbf{M}}{\mathbf{s}} = \frac{\mathbf{K}}{\triangle}$$

The value of the molecular depression constant of a solvent can be determined experimentally, using solutes

of known molecular weight, or it may be calculated theoretically from the relation

$$K = \frac{RT^2}{100L}$$

where R is the gas constant in calories, T the freezing-point of the solvent on the absolute scale, and L the latent heat of fusion of the solvent.

Table 2 gives the freezing points of a few common solvents, the experimental values of K, and also the values calculated from the latent heats of fusion.

TABLE 2.

MOLECULAR DEPRESSION OF THE FREEZING-POINT.

Solvent	Freezing-point	K (observed)	K (calculated)
Water	0°C	18·5°C	18·6°C
Benzene	5·5	51·2	50·7
Acetic acid	17	38·8	38·2
Phenol	39	53	50·5
Naphthalene	80	69	68·5
Camphor	175	400	...

Example 13. *3·29 gm. of a substance dissolved in 100 gm. of water* ($K=19$) *gave a depression of the freezing-point of 2·04°C. Find the molecular weight of the substance.* (*London Inter.* 1908.)

If M is the molecular weight of the substance, we have

$$\frac{M}{s} = \frac{K}{\triangle}$$

where $\triangle$ is the depression of the freezing-point produced by s gm. of the substance dissolved in 100 gm. of the solvent. In the present case

$$s = 3{\cdot}29 \text{ gm.}$$
$$K = 19$$
$$\triangle = 2{\cdot}04°.$$

Substituting these values in the above formula we get

$$M = \frac{19 \times 3{\cdot}29}{2{\cdot}04} = \mathbf{30{\cdot}6}.$$

Example 14. *The freezing-point of a solution containing* 20 *gm. of ammonium nitrate in* 100 *gm. of water is* $-6{\cdot}9°C$. *The freezing-point of a solution containing* 3·414 *gm. of cane-sugar in* 100 *gm. of water is* $-0{\cdot}185°C$. *Calculate the degree of dissociation of ammonium nitrate.* (*Punjab B.Sc.* 1916.)

Molecular weight of cane-sugar, $C_{12}H_{22}O_{11}$, is 342.

3·414 gm. of cane-sugar dissolved in 100 gm. of water cause a freezing-point depression of $0{\cdot}185°C$.

342 gm. of cane-sugar dissolved in 100 gm. of water will cause a depression of

$$0{\cdot}185 \times \frac{342}{3{\cdot}414} \text{ or } 18{\cdot}5°C.$$

Hence, the molecular depression constant of water is **18·5°**.

Now, molecular weight of ammonium nitrate, NH_4NO_3 is **80.**

Theoretical depression of freezing-point caused by 20 gm. of ammonium nitrate when dissolved in 100 gm. of water, assuming absence of dissociation

$$= 18{\cdot}5 \times \frac{20}{80} = 4{\cdot}6°$$

Observed depression $= 6{\cdot}9°$

Substituting these values in the formula (see Art. 15)

$$x = \frac{\triangle - \delta}{\delta(n-1)}$$

where x represents the degree of dissociation, n the number of ions into which a molecule of the electrolyte breaks up (*i.e.* 2 in this case), $\triangle$ the observed depression, and δ the theoretical depression, assuming no dissociation to have taken place, we get

$$x = \frac{6{\cdot}9 - 4{\cdot}6}{4{\cdot}6 \times (2-1)} = \mathbf{0{\cdot}50}.$$

The ammonium nitrate in the given solution is therefore 50% ionized.

Example 15. *The freezing-point of a solution of* 1 *gm. of a monobasic acid in* 100 *gm. of water was found to be* $-0^{\cdot}168^{\circ}$, *and* $0^{\cdot}200$ *gm. of the acid when dissolved and titrated required* $15^{\cdot}1$ *c.c. of N/10 alkali. Calculate the degree of ionization of the acid in the solution. The molecular depression for water is* $18^{\cdot}5$. (*Punjab B. Sc.* 1922.)

Amount of the acid neutralized by $15^{\cdot}1$ c.c. of N/10 alkali $= 0^{\cdot}200$ gm.

Amount of the acid neutralized by a litre of N alkali

$$= 0^{\cdot}200 \times \frac{1000}{15^{\cdot}1} \times 10 = 132 \text{ gm.}$$

Hence the equivalent weight of the acid, and also its molecular weight (since the acid is monobasic) = 132.

Theoretical depression of freezing-point caused by 1 gm. of the acid when dissolved in 100 gm. of water, assuming absence of dissociation

$$= 18^{\cdot}5 \times \frac{1}{132} = 0^{\cdot}140^{\circ}.$$

Observed depression $= 0^{\cdot}168^{\circ}$

Substituting these values in the formula

$$x = \frac{\triangle - \delta}{\delta (n-1)}$$

where x represents the degree of ionization, n the number, of ions into which a molecule of the acid breaks up (*i.e.* 2, since the acid is monobasic), $\triangle$ the observed depression and δ the theoretical depression, assuming absence of ionization, we get

$$x = \frac{0^{\cdot}168 - 0^{\cdot}140}{0^{\cdot}140 \times (2-1)} = \mathbf{0^{\cdot}200}.$$

Example 16. *The freezing-point of nitrobenzene is* $3^{\circ}C$. *A solution of* $1^{\cdot}20$ *gm. of chloroform in* 100 *gm. of nitrobenzene freezes at* $2^{\cdot}3^{\circ}C$. *A solution of* $0^{\cdot}6$ *gm. of acetic acid in* 100 *gm. of nitrobenzene freezes at* $2^{\cdot}64^{\circ}C$. ***From these data make what deductions you can concern-***

ing the molecular state of acetic acid when dissolved in nitrobenzene. (*Selwyn College, Cambridge.*)

Molecular weight of chloroform, $CHCl_3$, is 119·5.

1·20 gm. of chloroform dissolved in 100 gm. of nitrobenzene cause a freezing-point depression of

$$(3-2{\cdot}3)^\circ C. = 0{\cdot}7^\circ C.$$

119·5 gm. of chloroform dissolved in 100 gm. of nitrobenzene would produce a depression of

$$0{\cdot}7 \times \frac{119{\cdot}5}{1{\cdot}20} \text{ or } 69{\cdot}7^\circ.$$

Hence, the molecular depression constant of nitrobenzene is 69·7.

If M is the molecular weight of acetic acid in nitrobenzene, we have

$$\frac{M}{s} = \frac{K}{\triangle}$$

where $\triangle$ is the depression of the freezing-point produced by s gm. of the substance dissolved in 100 gm. of the solvent. In the case of acetic acid solution we have

$$s = 0{\cdot}6 \text{ gm.}$$

$$K = 69{\cdot}7$$

$$\triangle = 3 - 2{\cdot}64 = 0{\cdot}36^\circ$$

Substituting these values in the above equation we get

$$M = \frac{69{\cdot}7 \times 0{\cdot}6}{0{\cdot}36} = 116.$$

The normal molecular weight of acetic acid, CH_3COOH, is 60. Hence, in nitrobenzene solution the acid forms molecular complexes, each consisting of *two* simple molecules.

Example 17. *Calculate the osmotic pressure of an aqueous solution containing* 5·00 *gm. of dissolved substance per litre, given that the solution freezes at* $-0{\cdot}25^\circ C$. *The molecular lowering of the freezing point of water may be taken as* 18·5°C. (*Leeds Univ. Physical Chem.*)

Let M be the molecular weight of the dissolved substance. We have

$$\frac{M}{s} = \frac{K}{\triangle}$$

where $\triangle$ represents the depression of the freezing point produced by s gm. of the substance dissolved in 100 gm. of the solvent. In the present case we have

$$s = 5{\cdot}00 \times \frac{100}{1000} = 0{\cdot}500.$$

$$K = 18{\cdot}5^\circ$$

$$\triangle = 0{\cdot}25^\circ$$

Substituting these values in the above formula we get

$$M = \frac{18{\cdot}5 \times 0{\cdot}500}{0{\cdot}25} = 37.$$

37 gm. of the substance when present in 22·4 litres of solution at 0°C exert an osmotic pressure of 1 atmosphere.

Hence, 5·00 gm. of the substance, when present in 1 litre of solution at 0°, would exert an osmotic pressure of

$$1 \times \frac{5{\cdot}00}{37} \times \frac{22{\cdot}4}{1} \text{ or } \mathbf{3{\cdot}03 \text{ atmos.}}$$

EXERCISES

1. Calculate the osmotic pressure at 25°C. of a solution containing 5 gm. of urea in a litre of solution. *(Madras B.A.)*

2. The osmotic pressure of a 2 per cent solution of acetone in water is equal to 590 cm. of mercury at 10°C. What is the molecular weight of acetone ? *(Punjab B.Sc.)*

3. At 13°C the osmotic pressure of a solution containing 2·1 gm. of sucrose in 80 c.c. of the solution was 1·8 atmospheres. Calculate the molecular weight of sucrose and the value of the solution constant R.

4. What do the following results of Pfeffer suggest as to the molecular weight of gum-arabic ?

Grams per litre of the solution	Temperature	Osmotic pressure
9·9	15·5°C	7·0 cm. of mercury.
164·0	15·6°C	119·3 „ „ „

5. A solution containing 1·9 gram-molecules of calcium chloride per litre has the same osmotic pressure as a solution of cane-sugar containing 4·05 gram-molecules per litre. Find the degree of ionization of calcium chloride. (*London Inter. B. Sc.*)

6. The osmotic pressure of a solution of 0·184 gm. of urea in 100 c.c. of water was 56 cm. of mercury at 30°C. Calculate the molecular weight of urea, given the value of R in litre atm. units = 0·082. (*Bombay B.A.*)

7. A certain weight of a substance when in the gaseous state occupied a volume of 10 litres at 97°C. and 740 mm. pressure. The same weight of the substance when dissolved in 4·5 litres of water at 24°C. gave an osmotic pressure of 770 mm. of mercury. What explanation can you give of these facts? (*Oxford Higher School Cert.*)

8. The vapour pressure of ether at 20°C is 442 mm. and that of a solution of 6·1 gm. of benzoic acid, C_6H_5COOH, in 50 gm. of ether is 410 mm. at the same temperature. Calculate the molecular weight of benzoic acid in ether. (*Allahabad B. Sc.* 1930.)

9. Dry air was drawn in succession, first through a series of bulbs containing 4·257 gm. of a substance X in 52·68 gm. of ethyl alcohol, and then through a similar series of bulbs containing pure alcohol. The indrawn air and the two sets of bulbs were at the same temperature. The loss of weight in the first series of bulbs was 1·292 gm. and in the second series 0·0313 gm. Calculate the molecular weight of X. (*Pembroke College Cambridge.*)

10. Sodium nitrate is said to be dissociated to the extent of 64·9% in normal solution at 0°C. The molecular weight of water is 18·02 and its vapour pressure at 0°C is 4·62 mm. of mercury. The density of the normal solution is 1·063 gm. per c.c. at 0°C. What will be the vapour-pressure of the solution at this temperature? (*Manchester B. Sc.*)

11. The density of a 5 per cent solution of NaCl at 18°C is 1·0345. Calculate the vapour pressure of the solution at 18°C. The vapour pressure of pure water at this

temperature is 15·33 mm., and the NaCl in the solution is dissociated to the extent of 69·7 per cent.

(*London B. Sc. Hons.*, 1925.)

12. At 0°C. the vapour pressure of water is 4·62 mm. and that of a solution of 2·28 gm. of $CaCl_2$ in 100 gm. of water 4·584 mm. Calculate the degree of dissociation of the salt. (*London B. Sc.* 1926.)

13. A solution of 0·855 gm. of a metal in 100 gm. of mercury had, at a given temperature, a vapour pressure of 752·6 mm., that of pure mercury at the same temperature being 758 mm. Calculate the molecular weight of the metal, taking that of mercury as 200.

(*London B.Sc. Hons.* 1911.)

14. On distilling aniline in steam, 8·99 gm. of the liquid were carried over by 100 gm. of steam. The aqueous tension at the temperature of distillation (99·4°C) is 747 mm. The barometer stood at 760 mm. Calculate the molecular weight of aniline.

15. What weight of stearic acid will be carried over by 100 gm. of steam at 99°C., the atmospheric pressure being 753 mm. (Aqueous tension at 99° is 733 mm.)

16. 0·6 gram of a substance was dissolved in 10 grams of acetone. An elevation of 1·67°C. was observed in the boiling-point of the acetone. Calculate the molecular weight of the substance. (K for acetone = 1670).

(*Punjab B.Sc.* 1914.)

17. A solution containing 0·7269 gm. of camphor (molecular weight 152) in 32·08 gm. of acetone (boiling at 56·3°C) boiled at 56·55°C. What is the molecular elevation of boiling-point, and the latent heat of vaporization of oacetone? (*B. Sc.Sheffield.*)

18. The boiling point of ether is 35°C and a solution of one gram-molecule of a substance in 100 gm. of ether raises the boiling-point by 21°C. Calculate the latent heat of vaporization per gram of ether.

19. An aqueous solution of barium nitrate, containing 110·7 gram per litre, boils at 100·46°C. Calculate the

degree of dissociation of the salt. (Ba = 137·4 ; latent heat of steam = 536.) (*London B. Sc. Hons.*, 1925.)

20. On heating nitro-camphor ($C_{10}H_{15}NO_3$) only water is eliminated, and the other product gave the following results on analysis :—

0·3391 gm. gave 21·8 c.c. of moist nitrogen at 19° and 767 mm.

0·4332 gm. gave 28·2 of moist Nitrogen at 21° and 760 mm.

0·1650 gm. gave 0·3858 gm. of CO_2 and 0·1138 gm. of water.

The molecular weight was determined by the elevation of the boiling point of benzene :

2·8487 gm. raised the boiling point of 11·10 gm. of benzene 2·011°.

1·8842 gm. raised the boiling-point of 11·10 gm. of benzene 1·214°.

1·9012 gm. raised the boiling-point of 11·10 gm. of benzene 1·191°.

Molecular elevation of boiling-point for benzene = 26·7. What is the probable formula of the product ?

(*Lowry J.C.S.* 1898.)

21. A solution containing 0·5 gm. of a substance of molecular weight 182 dissolved in 42 gm. of benzene boils at 80·175°C. The boiling point of benzene is 80·000°C. What is its latent heat of evaporation ?

(*London B. Sc. Hons.*, 1922.)

22. State Raoult's law which governs vapour pressure and freezing-point of solutions. Apply the latter to calculate the molecular weight of a non-volatile substance from the following data :—

Weight of acetic acid taken	= 20·5 gm.
Freezing-point of acetic acid	= 16·435°C.
Weight of substance dissolved	= 0·1535 gm.
Freezing-point of solution	= 16·305°C.
Constant for acetic acid	= 38·6.

(*Allahabad M.A.* 1897.)

23. 2·167 and 2·833 gm. of a substance were dissolved in 100 gm. of benzene. The depressions of freezing-point were 0·348°C and 0·452°C respectively. What was the molecular weight of the substance ? The molecular lowering of freezing-point of benzene is 50°C.

(*Punjab B. Sc. Hons.* 1921.)

24. The freezing-point of a solution of 4 gms. of cadmium iodide in 95 c.c. of water is – 0·22°C. Calculate the apparent molecular weight of cadmium iodide. What does this suggest ? (*Punjab B. Sc.* 1932.)

25. A solution of 34·2 gm. of cane-sugar in 100 gm. of water froze at –1·9°; a solution of 7·5 gm. of potassium chlorate in 100 gm. of water froze at – 3·36° and a solution of 9·8 gm. of an unknown substance in 100 gm. of water froze at – 3·82°. The constant for water is 18·9°. What conclusions do you draw from these data concerning the molecular condition of the first two substances in aqueous solution, and what is the molecular weight of the unknown substance ? (*Bombay B.A.*)

26. The electrical conductivity of a 5 per cent solution of chromium trioxide is not increased by further dilution, and its freezing point is – 1·34°. What conclusions can you draw as to the condition in which the oxide exists in solution ? ($K = 19$.) (*Manc., B. Sc. Hons.*)

27. A solution contains 85·5 gm. of sucrose per 1000 gm. of water and is also N/100 with respect to HCl. Calculate as nearly as possible the freezing point (*i*) of the freshly prepared solution ; (*ii*) of the solution after half of the sucrose has been inverted. Molecular depression for 1 killogram of water is 1·858°. (*London B. Sc. Hons.* 1924.)

28. 6 gms. of anhydrous magnesium sulphate are dissolved in 100 gm. of water. The depression of the freezing-point is 0·901°C. If the constant for water in the case of the electrolyte is 37, what formula represents the state of hydration of the dissolved salt ?

(*Allahabad M. Sc.* 1902.)

29. 0·3691 gm. of a solid hydrocarbon gave on combustion 1·2773 gm. of CO_2 and 0·1866 gm. of H_2O. Also

0·1965 gm. of it in 12·6 gm. of benzene lowered the freezing-point of benzene by 0·44°C. Find the molecular formula of the hydrocarbon. (K for 100 gm. of benzene = 50.)

30. Calculate the latent heat of fusion of tin from the following data : Melting point of tin = 232°C. The depression of freezing-point for 1 gram atom of silver per 100 gram-atoms of tin is 3·0°C. (*London Hons.* 1907.)

31. The addition of 0·1407 gm. of mesitylene (C_9H_{12}) to 11·375 gm. of palmitic acid ($C_{15}C_{31}COOH$) lowered the freezing point of the latter from 62·25°C to 61·81°C. Find the latent heat of fusion per gm. of palmitic acid.
(*London B. Sc.* 1927.)

ANSWERS

1. 2·04 atmos. **2.** 59·8. **3.** 34·2; 84740.

4. 2544; 2474; mean, 2509. **5.** 56·5%. **6.** 62.

7. If x is the weight of the substance taken, molecular weight in the gaseous state is $3{\cdot}12x$ and in solution $5{\cdot}35x$. Hence we may conclude that either the vapour is dissociated or the substance exists as associated molecules in solution.

8. 127·1. **9.** 157·2. **10.** 4·48 mm. **11.** 14·92 mm.
12. 0.54. **13.** 238. **14.** 93·0. **15.** 43·0. **16.** 60.
17. 16·77°C; 129·3. **18.** 90·35 cals. **19.** 0·554.
20. $C_{20}H_{28}N_2O_5$. **21.** 92·5 cal. **22.** 312·8.
23. 311, 313, mean 312. **24.** 354.
25. 341, normal; 42·2, largely dissociated; 48·5.
26. $H^{\cdot} + H^{\cdot} + Cr_2O_7''$. **27.** 0·5018°; −0·734°.
28. $MgSO_4{\cdot}7H_2O$. **29.** $C_{14}H_{10}$.
30. 1700 cal. per gram-atom. **31.** 52·2 cal.

CHAPTER IV

LAW OF MASS ACTION

21. Law of Mass Action. This very important law, first enunciated by Guldberg and Waage of Christiania, may be stated as follows:—

The rate of a chemical reaction is directly proportional to the "active mass" of each of the interacting substances.

The term **active mass**, used in the enunciation of the law, means, in the case of gases and solutions, **molar concentration**, *i.e.*, the number of *mols* or gram-molecules present in a litre. The active mass of a solid reactant is always taken to be constant.

22. Application of the Law of Mass Action to a Balanced Action. Let us consider the reversible reaction

$$A + B \rightleftharpoons C + D$$

Suppose that the molar concentrations of the four substances at equilibrium are C_A, C_B, C_C and C_D respectively.

V_1, the velocity of the forward reaction at equilibrium $= k_1 \times C_A \times C_B$.

V_2, the velocity of the backward reaction at equilibrium $= k_2 \times C_C \times C_D$.

But $V_1 = V_2$

$$\therefore \quad \frac{C_C \times C_D}{C_A \times C_B} = \frac{k_1}{k_2} = K;$$

i.e., at the equilibrium point the product of the active masses of the resultants divided by the product of the active masses of the reactants is constant.

K is known as the **equilibrium constant**, k_1 and k_2 are called **affinity constants**, as they represent the measure of affinity of reactants for each other. Since the velocity of a reaction becomes equal to k_1 or k_2 when the concentration of the reactants is unity, they are also termed **velocity constants.**

Example 1. *In an experiment one gram-molecule of acetic acid was allowed to react with one gram molecule of ethyl alcohol until equilibrium was established. The equilibrium mixture was found to contain* 0·33 *gram-molecule of un-used acetic acid. Calculate the equilibrium constant of the reaction,*

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$$

If the volume of the reaction mixture is v litre, the active masses of the various substances at the equilibrium point are:—

Ethyl alcohol ... $\frac{1}{3v}$; Acetic acid ... $\frac{1}{3v}$;

Ethyl acetate ... $\frac{2}{3v}$; Water ... $\frac{2}{3v}$.

From the Law of Mass Action the equilibrium constant, K

$$= \frac{\left(\frac{2}{3v}\right)^2}{\left(\frac{1}{3v}\right)^2} \text{ or } \mathbf{4{\cdot}0}.$$

Example 2. *One gram-molecule of ethyl alcohol is mixed with four gram-molecules of acetic acid. Given that the equilibrium constant of the reaction*

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O,$$

is 4·0, *calculate the composition of the mixture at the equilibrium point.*

Let x mol be the quantity of ethyl acetate and of water produced at the equilibrium point. If v litre is the

total volume of the equilibrium mixture, the active masses of the four substances are :—

Ethyl alcohol ... $\frac{1-x}{v}$; Acetic acid ... $\frac{4-x}{v}$;

Ethyl acetate ... $\frac{x}{v}$; Water ... $\frac{x}{v}$.

From the Mass Action Law we have—

$$\frac{\left(\frac{x}{v}\right)^2}{\frac{1-x}{v} \times \frac{4-x}{v}} = 4$$

$$\therefore 3x^2 - 20x + 16 = 0$$

$$\therefore {}^{*}x = 0{\cdot}933.$$

Hence the equilibrium mixture consists of—

Ethyl alcohol	... 1 – 0·933 or	**0·067 mol**
Acetic acid	... 4 – 0·933 or	**3·067 mol**
Ethyl acetate	...	**0·933 mol**
Water	...	**0·933 mol**

23. First type Gas Reactions. First-type gas reactions are those in which the total number of molecules remains unaltered, and hence also the volume of the system at a given temperature and pressure. A typical example of the first-type gas reaction is the dissociation of hydriodic acid:—

$$2HI \rightleftharpoons H_2 + I_2$$

Suppose 1 gram-molecule of hydriodic acid is introduced into a vessel of volume V, and the temperature

---

*From Algebra we have :

If $ax^2 + bx + c = 0$,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

raised. Let x be the degree of dissociation at a certain temperature. Then the equilibrium concentrations are :--

$$[HI] = \frac{1-x}{V} \text{ mole per litre}$$

$$[H_2] = \frac{\frac{1}{2}x}{V} \quad ,, \quad ,,$$

$$[I_2] = \frac{\frac{1}{2}x}{V} \quad ,, \quad ,,$$

The dissociation constant, K, at the temperature of experiment is given by the expression

$$K = \frac{[H_2] \times [I_2]}{[HI]^2}$$

$$= \frac{\frac{x}{2V} \times \frac{x}{2V}}{\left(\frac{1-x}{V}\right)^2}$$

$$= \frac{x^2}{4(1-x)^2} \quad \ldots \quad \ldots \quad (1)$$

Let us now consider the reverse reaction. Suppose we start with a mols of hydrogen and b mols of iodine, the mixture occupying a volume of V litres, which remains constant throughout the experiment. Let equilibrium be established when x mols of H_2 and of I_2 have been converted into $2x$ mols of HI. Then the equilibrium concentrations are:

$$[H_2] = \frac{a-x}{V} \text{ mol per litre}$$

$$[I_2] = \frac{b-x}{V} \quad ,, \quad ,,$$

$$[HI] = \frac{2x}{V} \quad ,, \quad ,,$$

$$\therefore K = \frac{[H_2] \times [I_2]}{[HI]^2} = \frac{(a-x)(b-x)}{4x^2} \quad \ldots \quad (2)$$

It should be noted that in equations (1) and (2) the term V cancels out from the numerator and the denominator. Hence, in a first-type gas reaction, x depends merely on a, b and K, and is independent of the volume occupied by the reacting gases, and therefore also of the pressure.

Note. In gaseous reactions it has been found more convenient to express the active masses in terms of the *partial pressures* of the interacting gases than in mols per litre. In the former case the equilibrium constant is designated as Kp and in the latter as Kc. In a first-type gas reaction the value of Kp is *identical* with that of Kc.

Example 3. *When* 2·94 *mols of iodine and* 8·10 *mols of hydrogen are heated together at* 448°*C, it is found that* 5·64 *mols of hydrogen iodide are formed. How much hydrogen iodide would be present at equilibrium at the same temperature if we start with* 9·27 *mols of iodine and* 8·07 *mols of hydrogen? Also calculate the degree of dissociation of pure hydrogen iodide at* 448°*C.*

(1) CALCULATION OF THE EQUILIBRIUM CONSTANT.

The dissociation of hydrogen iodide into hydrogen and iodine is represented by the equation

$$2HI \rightleftharpoons H_2 + I_2$$

The molar concentrations of the three gases at equilibrium are :

$$[I_2] = 2{\cdot}94 - \frac{5{\cdot}64}{2} = 0{\cdot}12$$

$$[H_2] = 8{\cdot}10 - \frac{5{\cdot}64}{2} = 5{\cdot}28$$

$$[HI] = 5{\cdot}64$$

$$\therefore K = \frac{0{\cdot}12 \times 5{\cdot}28}{5{\cdot}64 \times 5{\cdot}64} = 0{\cdot}0199$$

(2) CALCULATION OF THE AMOUNT OF HYDROGEN IODIDE :

Let $2x$ mols of hydrogen iodide be produced at the equilibrium point when we start with a mols of hydrogen (=8·07) and b moles of iodine (=9·27).

Substituting the values of a, b and k in the equation

$$K = \frac{(a-x)(b-x)}{4x^2}$$

we have :

$$\frac{(8{\cdot}07-x)(9{\cdot}27-x)}{4x^2} = 0{\cdot}0199$$

Solving this quadratic equation (see foot-note, p. 76) we get

$$x = 12{\cdot}18 \text{ or } 6{\cdot}72$$

The former of these values is inadmissible, since in that case $a-x$ and $b-x$ will be negative. Hence the amount of hydrogen iodide at equilibrium

$$2x = 2 \times 6{\cdot}72 = \mathbf{13{\cdot}44 \text{ mols.}}$$

(3) CALCULATION OF THE DEGREE OF DISSOCIATION OF HYDROGEN IODIDE :

If x is the degree of dissociation of pure hydrogen iodide at 448°C, we have

$$\frac{x^2}{4(1-x)^2} = K$$

Substituting the value of K found in (1) we get

$$\frac{x^2}{4(1-x)^2} = 0{\cdot}0199$$

whence $x = 0{\cdot}220$ or $-0{\cdot}393$.

The negative value of x is, of course, impossible. Hence, the degree of dissociation of hydrogen iodide at 448°C is **0·220** or **22·0%**

Example 4. *A sample of HI was found to be 22·0% dissociated when equilibrium was reached. What will be the degree of dissociation if (a) hydrogen, (b) argon is add-*

ed in the proportion of 1 *mol for every mol of HI originally present, the temperature and pressure of the system being kept constant?* (*Manchester, Gen. Sci. Hons. Finals.*)

The dissociation of hydrogen iodide into hydrogen and iodine is represented by the equation

$$2HI \rightleftharpoons H_2 + I_2$$

Since at the given temperature and pressure HI is 22·0 per cent dissociated, the molar concentrations of the three gases at equilibrium are:

$$[HI] = 100 - 22{\cdot}0 = 78{\cdot}0$$

$$[H_2] = \frac{22{\cdot}0}{2} = 11{\cdot}0$$

$$[I_2] = \frac{22{\cdot}0}{2} = 11{\cdot}0$$

$$\therefore K = \frac{11{\cdot}0 \times 11{\cdot}0}{78{\cdot}0 \times 78{\cdot}0} = 0{\cdot}0199$$

(*a*) When we start with a mixture of 1 mol of HI and 1 mol of H_2, let x be the degree of dissociation of HI. The equilibrium molar concentrations are

$$[I_2] = \frac{x}{2}$$

$$[H_2] = 1 + \frac{x}{2}$$

$$[HI] = 1 - x$$

Substituting these values and the value of K in the mass law equation

$$\frac{[H_2][I_2]}{[HI]^2} = K$$

we get

$$\frac{\frac{x}{2} \times \left(1 + \frac{x}{2}\right)}{(1-x)^2} \; 0{\cdot}0199$$

whence $x = 0{\cdot}037$ or $-2{\cdot}4$.

Since the negative value of x is impossible, the degree of dissociation of hydrogen iodide, when mixed with an equi-molar quantity of hydrogen, is

0·037 or **3·7%**

(*b*) The dissociation of HI is a first-type gas reaction (Art. 23), so the addition of a gas, such as argon, which takes no part in the reaction, has no effect on the equilibrium point. Hence the degree of dissociation in this case will be the same as that of pure hydrogen iodide, *i.e.*, **22·0%**.

24. Second-type Gas Reactions. In this case there occurs a change in the total number of molecules in the system during the reaction and hence in the volume or pressure of the gas. Therefore, for the investigation of a second-type gas reaction, vapour density determination is frequently employed. The degree of dissociation, x, is given by the relation

$$x = \frac{D-d}{d(n-1)}$$

where D is the density of the undissociated gas and d that of the dissociated gas. (See Art. 11).

A typical example of the second-type gas reaction is the dissociation of *phosphorus pentachloride*:—

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Suppose 1 gram-molecule of phosphorus pentachloride is introduced into a vessel of volume V, and x is the degree of dissociation at the given temperature. Then the equilibrium concentrations are

$$[PCl_5] = \frac{1-x}{V} \text{ mol per litre}$$

$$[PCl_3] = \frac{x}{V} \quad ,, \quad ,,$$

$$[Cl_2] = \frac{x}{V} \quad ,, \quad ,,$$

The dissociation constant, Kc, at the temperature of the experiment is given by the expression

$$Kc = \frac{[PCl_3] \times [Cl_2]}{[PCl_5]}$$

$$= \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{1-x}{V}}$$

$$= \frac{x^2}{(1-x)V} \quad \ldots \quad \ldots \quad (3)$$

Hence, the dissociation constant, Kc may be calculated from the degree of dissociation, x, which in turn is found from vapour density determination. The volume V is expressed in litres occupied by a gram-molecule of the gas at the temperature of reaction. It is given by the relation

$$V = 22{\cdot}4(1+x) \times \frac{273+t}{273} \times \frac{1}{P} \quad \ldots \quad \ldots \quad (4)$$

(since it is directly proportional to the total number of molecules present and to the absolute temperature, and inversely proportional to the pressure).

Let us now express the active masses of the three gases in terms of partial pressures. Suppose we start with 1 gram-molecule of PCl_5, the degree of dissociation at equilibrium being x and the total pressure of the system P. If p_1 is the partial pressure of PCl_5 and p_2 that of PCl_3 and of Cl_2, we have

$$p_1 + 2p_2 = P$$

and

$$Kp = \frac{p_2^2}{p_1}$$

Now, at equilibrium, there are in all $1-x+2x$, *i.e.* $1+x$ gram-molecules. Since the pressure is proportional to the

number of mols at constant volume, p_1 and p_2, when expressed in terms of x and P, are given by the equations

$$p_1 = \frac{1-x}{1+x} P$$

$$p_2 = \frac{x}{1+x} P$$

$$\therefore Kp = \frac{\frac{x^2}{(1+x)^2} \times P^2}{\frac{1-x}{1+x} \times P} = \frac{x^2 P}{(1+x)(1-x)} \quad \ldots \qquad (5)$$

From equations (3) and (5) we see that the degree of dissociation, x, in a second type gas reaction varies with the volume and consequently with the pressure of the system.

Another important example of the second-type gas reaction is the dissociation of **nitrogen peroxide** :—

$$N_2O_4 \rightleftharpoons 2NO_2$$

Here the equilibrium concentrations are

$$[N_2O_4] = \frac{1-x}{V}$$

$$[NO_2] = \frac{2x}{V}$$

$$\therefore Kc = \frac{4x^2}{(1-x)V} \quad \ldots \qquad \ldots \qquad (6)$$

The partial pressures of the two molecular species are

$$pN_2O_4 = \frac{1-x}{1+x} P$$

$$pNO_2 = \frac{2x}{1+x} P$$

$$\therefore Kp = \frac{4x^2 P}{(1+x)(1-x)} \quad \ldots \qquad \ldots \qquad (7)$$

Example 5. *At 49·7° and under a pressure of* 182 *mm. of mercury the density of nitrogen peroxide was* 1·89

whilst that of the undissociated peroxide was 3·18 [*air* = 1]. *Calculate the degree of dissociation and the dissociation constant. At what pressure would the mixture be half dissociated ?* [*Wt. of* 1 *litre of air at N.T.P.* = 1·293 *gm.*] (*London B.Sc.*)

(*a*) CALCULATION OF THE DEGREE OF DISSOCIATION:

Observed density, d, of nitrogen peroxide at 49·7° and 182 mm. = 1·89.

Density, D, of undissociated nitrogen peroxide = 3·18.

From the equation

$$N_2O_4 \rightleftharpoons 2NO_2$$

we see that the number of simpler molecules, n, into which a molecule of nitrogen peroxide splits up = 2.

Substituting these values in the formula

$$x = \frac{D-d}{d(n-1)} \qquad \text{[Art. 11.}$$

we get :

The degree of Dissociation of nitrogen peroxide at 49·7° and 182 mm.

$$= \frac{3{\cdot}18-1{\cdot}89}{1{\cdot}89(2-1)}$$

$$= 0{\cdot}683.$$

(*b*) CALCULATION OF THE DISSOCIATION CONSTANT, *Kc*:—

Since 1 litre of air at N.T.P. weighs 1·293 gm., the weight of 1 litre of nitrogen peroxide at 49·7° and 182 mm.

$$= 1{\cdot}293 \times \frac{182}{760} \times \frac{273}{273+49{\cdot}7} \times 1{\cdot}89 \text{ gm.}$$

$$= 0{\cdot}4952 \text{ gm.}$$

Out of this, there is 0·4952 × 0·683 gm., or 0·3383 gm. of NO_2 and 0·4952 − 0·3383 gm., or 0·1569 gm. of N_2O_4.

Molar concentrations of the two kinds of molecules are:

$$[NO_2] = \frac{0{\cdot}3383}{46}$$

$$[N_2O_4] = \frac{0{\cdot}1569}{92}$$

$$\therefore\ Kc = \frac{0{\cdot}3383 \times 0{\cdot}3383 \times 92}{46 \times 46 \times 0{\cdot}1569}$$

$$= \mathbf{0{\cdot}03171}$$

(*c*) CALCULATION OF THE PRESSURE AT WHICH THE GAS WOULD BE HALF-DISSOCIATED :—

The dissociation constant Kp is given by the expression (Art. 24, Formula 7):—

$$Kp = \frac{4x^2 P}{(1+x)\,(1-x)}$$

Substituting the values of x and p in the expression we get

$$Kp = \frac{4 \times 0{\cdot}683 \times 0{\cdot}683 \times 182}{1{\cdot}683 \times 0{\cdot}317} = 636$$

To get the pressure at which the gas would be one-half dissociated, we substitute in the above formula the values of Kp (*i.e.*, 636) and of x (*i.e.*, 0·5). Thus we get

$$\frac{4 \times P \times 0{\cdot}5 \times 0{\cdot}5}{1{\cdot}5 \times 0{\cdot}5} = 636$$

whence $P = 477$.

Hence the pressure at which nitrogen peroxide would be one-half dissociated at 49·7° is **477 mm.**

Example 6. *Nitrogen tetroxide dissociates according to the equation*

$$N_2O_4 \rightleftharpoons 2NO_2$$

At O°C and atmospheric pressure, the mixture has a density of 41·0 (*referred to* $H = 1$ *at N.T.P.*). *Calculate*

(a) the degree of dissociation, and (b) the density, at 0°C and 0·5 atmosphere pressure.

(Manchester, Gen. Sci. Hons. Finals.)

(*a*) CALCULATION OF THE DEGREE OF DISSOCIATION:—

Theoretical density, D, of undissociated nitrogen tetroxide (referred to H = 1 at N.T.P.)

$$= \frac{28+64}{2} = 46$$

Observed density, d, of the gas at N.T.P. = 41·0.

Number of simpler molecules, n, into which a molecule of N_2O_4 splits up = 2.

Substituting these values in the formula

$$x = \frac{D - d}{d(n - 1} \qquad [Art. 11.$$

we get x, the degree of dissociation of nitrogen tetroxide at N.T.P.

$$x = \frac{46 - 41{\cdot}0}{41{\cdot}0(2 - 1)}$$

$$= 0{\cdot}122$$

The value of the dissociation constant, Kp, is given by the expression (Art. 24, Formula 7)

$$Kp = \frac{4x^2P}{(1+x)(1-x)}$$

$$= \frac{4 \times 0{\cdot}122 \times 0{\cdot}122 \times 1}{1{\cdot}122 \times 0{\cdot}878}$$

$$= 0{\cdot}06345$$

The degree of dissociation x_1, at 0°C and 0·5 atmosphere pressure is given by the expression

$$Kp = \frac{4x_1^2P}{(1+x_1)(1-x_1)}$$

$$\therefore\ 0{\cdot}06045 = \frac{4x_1^2 \times 0{\cdot}5}{(1+x_1)(1-x_1)}$$

whence $$x_1 = \mathbf{0{\cdot}1713}$$

(*b*) CALCULATION OF DENSITY AT 0°C AND 0·5 ATMOSPHERE PRESSURE:—

Volume occupied by a gram-molecule of the gas at 0°C and 0·5 atmosphere pressure

$$= 22{\cdot}4(1 + x_1) \times \frac{1}{0{\cdot}5} \text{ litres}$$

$$= 22{\cdot}4 \times 1{\cdot}1713 \times \frac{1}{0{\cdot}5} \text{ litres}$$

$$= 52{\cdot}47 \text{ litres.}$$

Density of the gas at 0°C and 0·5 atmosphere pressure

$$= 46 \times \frac{22{\cdot}4}{52{\cdot}47} = \mathbf{19{\cdot}6.}$$

25. Heterogeneous Reactions. The law of mass-action applies not only to a homogeneous system (gas or solution) but also to the gaseous or the solution phase of a gas-solid system, the concentration of the solid in the gaseous phase (*i.e.* its vapour pressure) is constant at a given temperature. Similarly, in the case of a liquid soild system, the concentration of the solid in the solution phase (*i.e.* its solubility) is constant as long as the temperature remains unaltered. These constant concentrations of the solid components may be included in K, the equilibrium constant.

Let us consider the heterogeneous reaction

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

The law of mass-action applies only to the gaseous phase. Representing the active masses of the various components by their partial pressures we have

$$K = \frac{(p Fe_3O_4) \times (p H_2)^4}{(p Fe)^3 \times (p H_2O)^4}$$

Since $p Fe_3O_4$ and $p Fe$ are constant at a given temperature, we can have the simplified expression

$$K' = \frac{p H_2}{p H_2O}$$

Thus we see that the partial pressures of hydrogen and steam will remain constant so long as the tempera-

ture remains constant, and will be independent of the solid components present.

Example 7. *In the reaction*

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

equilibrium is found to be established at 200°C *when the partial pressure of steam is* 46 *mm. and that of hydrogen* 960 *mm. Calculate the pressure of steam at equilibrium when that of hydrogen is* 2000 *mm.*

The equilibrium constant K

$$= \frac{p\,H_2}{p\,H_2O} = \frac{960}{46} = 20{\cdot}9$$

When the partial pressure of hydrogen is 2000 mm., let that of steam be x mm. We have

$$\frac{2000}{x} = 20{\cdot}9$$

$$\therefore x = 95{\cdot}7$$

Hence the required partial pressure of steam is **95·7 mm.**

EXERCISES

1. Equivalent weights of ethyl acetate and water were heated in a sealed tube until no further change took place in the composition of the mixture. It was found on titration that $^1/_3$ of an equivalent of acetic acid had been produced. What weight of acetic acid would be obtained on heating a mixture of 10 gm. of ethyl acetate and 4 gm. of water in the same way? (*Punjab B.Sc.*)

2. While investigating the reaction between acetic acid and alcohol the following figures were abtained by Berthelot and Pean de St. Gilles:—

Mol. acetic acid taken	*Mol. alcohol taken*	*Mol. ester formed*
1·0	0·05	0·05
1·0	0·18	0·171
1·0	0·33	0·293
1·0	0·50	0·414
1·0	1·00	0·667
1·0	2·00	0·858
1·0	8·00	0·966

What conclusion can be drawn from these results ?
(*Punjab B.Sc.* 1928.)

3. In four experiments in which one gram-molecule of acetic acid was allowed to react with the following different quantities (x gram-molecules) of ethyl alcohol, until equilibrium was established, Berthelot and Pean de Saint Gilles found that the following amounts of ethyl acetate (y gram-molecules) were produced:—

	(*i*)	(*ii*)	(*iii*)	(*iv*)
x...	0·5	1·0	2·0	12·0
y...	0·42	0·66	0·83	0·98

Show that these results are in accord with the law of Guldberg and Waage. (*Vict., B.Sc. Hons.*)

4. Amylene and trichloracetic acid react to form an ester according to the equation

$$CCl_3.COOH + C_5H_{10} \rightleftharpoons CCl_3.COOC_5H_{11}$$

In an experiment at 100°C, the equilibrium mixture contained 3·846 gram-molecules of amylene per litre, 0·6594 gram-molecules of acid per litre, and 2·111 gram-molecules of ester per litre. What concentration of ester is obtained if a mixture containing initially 1 gram-molecule of acid and 4·48 gram-molecules of amylene in 638 c.c. is allowed to proceed to equilibrium at the same temperature? (*Liverpool, B.Sc.*)

5. Bodenstein found that at 443°C the dissociation of hydrogen iodide according to the equation

$$2HI \rightleftharpoons H_2 + I_2$$

was 21·98 per cent. For experiments at the some temperature, starting with varying amounts of hydrogen and iodine, the amount of hydrogen iodide present when equilibrium was attained is given by the following numbers:—

Iodine (c.c. *vapour*)	*Hydrogen* (c.c.)	*Hydrogen Iodide* (c.c.)
Initial	*Initial*	*Found*
2·94	8·10	5·66
9·27	8·07	13·34
33·10	7·89	15·12

Calculate from the first two columns the amounts of hydrogen iodide predicted by the Law of Mass Action, and compare them with experimental figures.

(*Punjab B.Sc. Hons.* 1913.)

6. If nitrogen peroxide is one-half dissociated under certain conditions, what proportion will remain undissociated when the volume is increased to 10 times the original value while the temperature remains the same.

(*Manchester, Hons.* 1910.)

7. The following table gives the density, referred to air, of nitrogen peroxide at the pressure shown and at a temperature of 50°C :—

Pressure in mm.	*Relative Density*
26·8	1·66
93·8	1·79
182·7	1·89
261·4	1·96
497·8	2·15

The relative density calculated for N_2O_4 at this temperature is 3·20. Show how far the figures support the Law of Mass Action for the equilibrium

$$N_2O_4 \rightleftharpoons 2NO_2$$

(*Punjab B.Sc.* 1925.)

8. At 730°C the vapour density of iodine under a pressure of 1 atmosphere is 97·45% of the theoretical, on the assumption that the molecule of gaseous iodine is diatomic. What is the degree of dissociation of iodine under these conditions? Calculate the equilibrium constant, Kp, of the reaction

$$I_2 \rightleftharpoons 2I$$

and find what the degree of dissociation of iodine would be at 730°C under a pressure of 0·1 atmosphere.

(*Liverpool, B.Sc.*)

9. At 630°C and 1 atmosphere, sulphur trioxide is just one-third dissociated. Calculate the dissociation

constant of sulphur trioxide in terms of partial pressures.
(*Liverpool, B.Sc.*)

ANSWERS

1. 3·09 gm.
3. K = (*i*) 3·8, (*ii*) 3·8, (*iii*) 3·5, (*iv*) 4·4.
4. 1·295 mol of ester per litre.
5. 5·64 ; 13·47 ; 15·40. **6.** 14·6%.
8. 0·0262 ; Kp = 0·00274; 0·082.
9. 0·0357.

CHAPTER V

VELOCITY OF REACTION

26. General. Most of the reactions in Inorganic Chemistry, specially those with which a student becomes familiar during his analytical work, take place instantaneously. But there are reactions, like the decomposition of hydrogen peroxide (in the presence of a catalyst), which proceed with measurable velocity. In Organic Chemistry, the reactions, as a rule, are not ionic, and, consequently, take place with a velocity which can be measured experimentally.

While it is possible to measure the rate of an irreversible chemical change, in reversible reactions what we can actually measure is the difference between the rates of the opposing actions. It is on this account that the reactions of the former type alone are suitable for a study of the reaction velocity.

27. Order of a Reaction. From the study of the velocity of a reaction, it is possible to determine what is generally called the "order of the reaction," or the number of molecules that participate in the change. When one molecule takes part in a change, the reaction is called *monomolecular* or *reaction of the first order*, when two or three molecules take part, the reaction is said to be *bi-* or *tri molecular*, or that of the 2nd or 3rd order.

28. Monomolecular Reactions. If a represents the initial concentration of a substance undergoing a monomolecular change, and $(a-x)$ its concentration after the expiry of t minutes, then the velocity of decomposition of the substance just after the expiry of t minutes will be equal to $\frac{dx}{dt}$ where dx represents a very small quantity that

has changed during a very small interval of time dt. By the law of mass action, the velocity $\frac{dx}{dt}$ must be equal to $k(a-x)$, where k is the velocity constant and $(a-x)$ the concentration of the substance at the time t:—

$$\frac{dx}{dt} = k\,(a-x) \qquad \ldots \qquad (1)$$

This is a differential equation, which, on integration, becomes

$$K = \frac{1}{t}\log_e \frac{a}{a-x} \qquad \ldots \qquad (2)$$

or
$$0{\cdot}4343K = \frac{1}{t}\log_{10} \frac{a}{a-x} = K' \qquad \ldots \qquad (3)$$

This equation represents the relation of t, a, and x for monomolecular reactions, and, by its application, constant values of k should be obtained for all values of t, a and x.

In a monomolecular reaction, the time required for the completion of the same fraction of the change is the same whatever be the value of the initial concentration a.

Example 1. *From the following data show that the decomposition of H_2O_2 in aqueous solution is a monomolecular reaction:—*

Time in Minutes	0	10	20
N	22·8	13·8	8·25 c.c.

where N is the number of c.c. of $KMnO_4$ required to decompose a definite volume of the H_2O_2 solution.

(*Punjab B.Sc. Hons.* 1921.)

a in terms of c.c. of $KMnO_4 = 22{\cdot}8$

$(a-x)$ „ „ „ $= 13{\cdot}8$ and 8.25

$$K' = \frac{1}{t}\log\frac{a}{a-x}$$

$$= \frac{1}{10}\log\frac{22{\cdot}8}{13{\cdot}8} = {\cdot}02180$$

$$K' = \frac{1}{20} \log \frac{22{\cdot}8}{8{\cdot}25} = {\cdot}02207$$

We find that the values of K′ are practically constant and the reaction is therefore of the first order.

Example 2. *A dilute solution of cane sugar was hydrolyzed into glucose and fructose by the addition of dilute hydrochloric acid. The progress of the reaction was followed in a polarimeter tube by observing the angles of rotation at various times. The following results were obtained:—*

Time (in minutes)	0	10	20	30	40	80	∞
Angle of Rotation	+32·4°	28·8°	25·5°	22·4°	19·6°	10·3°	−14·1°

Show that the reaction is monomolecular and calculate the time required for the completion of half the change.

(*a*) To show that the Reaction is Monomolecular.

The rotation that corresponds to cent per cent. change $= 32{\cdot}4 - (-14{\cdot}1) = 46{\cdot}5°$

$\therefore$ a may be taken $= 46{\cdot}5$

$(a-x)$ for various intervals of time will be :—

t	$(a-x)$
10	$46{\cdot}5 - (32{\cdot}4 - 28{\cdot}8) = 42{\cdot}9$
20	$46{\cdot}5 - (32{\cdot}4 - 25{\cdot}5) = 39{\cdot}6$
30	$46{\cdot}5 - (32{\cdot}4 - 22{\cdot}4) = 36{\cdot}5$
40	$46{\cdot}5 - (32{\cdot}4 - 19{\cdot}6) = 33{\cdot}7$
80	$46{\cdot}5 - (32{\cdot}4 - 10{\cdot}3) = 24{\cdot}4$

The equation for a monomolecular reaction is

$$K' = \frac{1}{t} \log_{10} \frac{a}{a-x}$$

$$\therefore K' = \frac{1}{10} \log \frac{46{\cdot}5}{42{\cdot}9} = {\cdot}00350$$

$$= \frac{1}{20} \log \frac{46{\cdot}5}{39{\cdot}6} = {\cdot}00349$$

$$= \frac{1}{30} \log \frac{46{\cdot}5}{36{\cdot}5} = {\cdot}00350$$

$$= \frac{1}{40} \log \frac{46{\cdot}5}{33{\cdot}7} = {\cdot}00349$$

$$= \frac{1}{80} \log \frac{46{\cdot}5}{24{\cdot}4} = {\cdot}00350.$$

The values of K' obtained are practically constant. Therefore the reaction is *monomolecular*.

(*b*) To calculate the Time required for the Completion of Half the Change.

Time required for completing half the change can be calculated from the equation

$$K' = \frac{1}{t} \log \frac{1}{\frac{1}{2}}$$

$${\cdot}0035 = \frac{1}{t} \log 2 = \frac{1}{t} \times 0{\cdot}3010$$

whence $t = \mathbf{86}$ **minutes.**

Example 2. *What is meant by the "velocity co-efficient" of a chemical reaction? When a solution of dibromo-succinic acid is heated, the acid decomposes as follows:—*

$$C_2H_2Br_2(COOH)_2 = C_2HBr(COOH)_2 + HBr$$

A given solution of dibromo succinic acid was kept at 70°C *and a definite volume titrated with standard alkali from time to time. The following results were obtained:—*

Time in minutes	0	360	840
Alkali required for neutralization	20·19	23·34	26·07 c.c.

(*a*) *Calculate the velocity co-efficient of the reaction.*

(*b*) *After what time, from the commencement of the experiment, is one half of the dibromo-succinic acid decomposed?*

[$\log_e 10 = 2{\cdot}3026$] (*Manchester, Gen. Sci. Hons. Finals.*)

(*a*) Calculation of the Velocity Coefficient.

One molecule of dibasic dibromo-succinic acid produces, on decomposition, one molecule of bromomaleic acid, which is also dibasic, and one molecule of monobasic hydrobromic acid. Therefore, before decomposition, each molecule of the acid will require for its neutralization 2 equivalents of the alkali, while after decomposition it will require 3 equivalents.

a in terms of c.c. of alkali $= 20{\cdot}19$

x can be calculated from the following reasoning:—

Let the undecomposed dibromo-succinic acid neutralize $(20{\cdot}19 - x)$ c.c. The decomposed portion will produce quantities of bromo-maleic acid and hydrobromic acid which will neutralize x c.c. and $x/2$ c.c. of the alkali respectively.

$$\therefore \quad (20{\cdot}19 - x) + x + \tfrac{1}{2}x = 23{\cdot}34$$

or $$x = 6{\cdot}3$$

Similarly, x at the second interval of time

$$= 2 \times (26{\cdot}07 - 20{\cdot}19) = 11{\cdot}76$$

$$\therefore \quad K' = \frac{1}{360} \log \frac{20{\cdot}19}{20{\cdot}19 - 6{\cdot}3} = {\cdot}00045$$

$$= \frac{1}{840} \log \frac{20{\cdot}19}{20{\cdot}19 - 11{\cdot}76} = {\cdot}00045$$

$$K = {\cdot}00045 \times 2{\cdot}3026 = \mathbf{{\cdot}001036}$$

(*b*) Calculation of the Half-Change Period.

Time t required for the half change can be calculated from the equation

$$K' = \frac{1}{t} \log 2$$

$$\therefore \quad {\cdot}00045 = \frac{1}{t} \times 0{\cdot}3010$$

whence $$t = \mathbf{668{\cdot}9 \text{ minutes.}}$$

Example 4. *The following figures have been obtained for the pressure of the gas in a vessel which contained phosphine, decomposing under the influence of heat. It gives the time at which the pressure in the vessel is equal to p:—*

$t=0$	4	14	24	46·3
$p=758{\cdot}01$	769·34	795·57	819·16	865·22

From these figures determine what formula best represents the reaction. (*Punjab B.Sc. Hons.* 1918.)

From the equation

$$2PH_3 \rightleftharpoons 2P + 3H_2$$

we see that the pressure after decomposition becomes $1\frac{1}{2}$ if the gas is heated in a closed vessel, *i.e.*, if the volume be kept constant.

The value of x, *i.e.*, the amount of phosphine decomposed at any interval of time can be calculated from the initial pressure and the pressure at that instant.

Thus, the value of x, after 4 minutes from the commencement of the reaction, is given by the equation

$$758{\cdot}01\left(1-x+\frac{3}{2}x\right)=769{\cdot}34$$

whence $$x={\cdot}0298$$

Similarly,

when $t=14$ mins. $x={\cdot}0991$
when $t=24$ mins. $x={\cdot}1614$
when $t=46{\cdot}3$ mins. $x={\cdot}2828$

Taking $a=1$ and x equal to the above values at the given times, we get the following values of K' by the use of the equation of the first order

$$\frac{1}{t}\log\frac{a}{a-x}=K'$$

$$(i)\ \frac{1}{4}[\log 1 - \log (1 - 0{\cdot}0298)] = K'$$

whence $K' = {\cdot}00327$

$$(ii)\ \frac{1}{14}[\log 1 - \log (1 - 0{\cdot}0991)] = K'$$

whence $K' = {\cdot}00324$

$$(iii)\ \frac{1}{24}[\log 1 - \log (1 - 0{\cdot}1614)] = K'$$

whence $K' = {\cdot}00319$

$$(iv)\ \frac{1}{46{\cdot}3}\ [\log 1 - \log (1 - 0{\cdot}2828)] = K'$$

whence $K' = {\cdot}00312$

The values of K' obtained are constant within the limits of experimental error. Therefore the reaction is best represented by the formula for a monomolecular reaction.

29. Bimolecular Reactions. In a bimolecular reaction,

$$A + B \longrightarrow C + D,$$

if a and b represent the initial concentrations and $a - x$ and $b - x$ the concentrations of the reactants after the expiry of t minutes, then the reaction velocity of the change just after the expiry of t minutes will be

$$\frac{dx}{dt} = K(a - x)(b - x) \qquad \ldots \qquad (4)$$

If the initial concentration of both the reactants be a, then the equation will become

$$\frac{dx}{dt} = K(a - x)^2 \qquad \ldots \qquad (5)$$

This by integration gives

$$\mathbf{K = \frac{1}{t} \times \frac{x}{a(a - x)}} \qquad \ldots \qquad (6)$$

If the initial concentrations of the reactants are equal, *i.e.*, a remains the same, the above relation becomes simpler, *viz.*

$$\mathbf{K' = \frac{1}{t} \times \frac{x}{a - x}} \quad \ldots \quad (7)$$

where $$K' = \frac{K}{a}$$

In a bimolecular reaction the time required for the completion of the same fraction of the change is inversely proportional to the initial concentration.

Note. When the initial concentrations of the reactants are not equal, the equation becomes more complicated, and is expressed as under:—

$$K = \frac{1}{t(a-b)} \times \log_e \frac{b(a-x)}{a(b-x)}$$

$$\therefore 0{\cdot}4343K = \frac{1}{t(a-b)} \times \log_{10} \frac{b(a-x)}{a(b-x)}$$

$$K' = \frac{1}{t(a-b)} \times \log 10 \frac{b(a-x)}{a(b-x)}$$

Example 5. *When ethyl acetate is saponified by sodium hydroxide, the progress of the reaction can be measured by periodically titrating the unchanged alkali against a standard acid. Using equal concentrations of ester and alkali, the following results were obtained in an experiment :—*

t in minutes	0	5	25	55	120	∞
c.c. *of acid* $(a-x)$	16	10·24	4·32	2·31	1·1	0

Show that the reaction is bimolecular. What fraction of the ethyl acetate will be decomposed in 30 *minutes ?*

(*a*) To show that the Reaction is Bimolecular

The equation for bimolecular reactions is

$$\frac{1}{t} \times \frac{x}{(a-x)} = K'$$

$$\text{First value of } K' = \frac{1}{5} \times \frac{5{\cdot}76}{10{\cdot}24} = 0{\cdot}112$$

$$\text{Second} \quad ,, \quad ,, \quad = \frac{1}{25} \times \frac{11{\cdot}68}{4{\cdot}32} = 0{\cdot}108$$

$$\text{Third} \quad ,, \quad ,, \quad = \frac{1}{55} \times \frac{13{\cdot}69}{2{\cdot}31} = 0{\cdot}108$$

$$\text{Fourth} \quad ,, \quad ,, \quad = \frac{1}{120} \times \frac{14{\cdot}9}{1{\cdot}1} = 0{\cdot}113$$

The values are practically constant, therefore the reaction is of the second order.

(*b*) To calculate the Fraction of Ethyl Acetate Decomposed in 30 Minutes.

The amount of ethyl acetate decomposed in 30 minutes can be calculated from the equation

$$0{\cdot}110 = \frac{1}{30} \times \frac{x}{(16 - x)}$$

whence $x = 12{\cdot}3.$

$\therefore$ The fraction of the ethyl acetate decomposed in 30 minutes $= \frac{12{\cdot}3}{16} = \mathbf{0{\cdot}77}.$

Example 6. *Acetamide is hydrolyzed when treated with hydrochloric acid in aqueous solution according to the equation*

$$CH_3.CO.NH_2 + H_2O + HCl \longrightarrow CH_3COOH + NH_4Cl$$

The reaction can be followed by withdrawing and treating a definite volume of the reaction mixture with an alkaline solution of sodium hypobromite and measuring the volume of nitrogen evolved. The results of an experiment are given in the following table. The volume of nitrogen given off is equivalent to the amount of unchanged amide in the reaction mixture :—

t = (*time in minutes*).	0	15	30	45	60	75	90
n = (*volume of nitrogen in c.c. reduced to N.T.P.*)	26·80	22·38	19·27	16·64	14·67	13·12	11·83

Show that the reaction is bimolecular.

SOLUTION :—

a in terms of c.c. of nitrogen at N.T.P. = 26·80.
$(a - x)$,, ,, ,, ,, = values given

By applying the equation for bimolecular reactions, we get the following values of K' :—

(*i*) $\frac{1}{15} \times \frac{26{\cdot}80 - 22{\cdot}38}{22{\cdot}38} = K'$ $\therefore K' = {\cdot}01317$

(*ii*) $\frac{1}{30} \times \frac{26{\cdot}80 - 19{\cdot}27}{19{\cdot}27} = K'$ $\therefore K' = {\cdot}01303$

(*iii*) $\frac{1}{45} \times \frac{26{\cdot}80 - 16{\cdot}64}{16{\cdot}64} = K'$ $\therefore K' = {\cdot}01355$

(*iv*) $\frac{1}{60} \times \frac{26{\cdot}80 - 14{\cdot}67}{14{\cdot}67} = K'$ $\therefore K' = {\cdot}01379$

(*v*) $\frac{1}{75} \times \frac{26{\cdot}80 - 13{\cdot}12}{13{\cdot}12} = K'$ $\therefore K' = {\cdot}01390$

(*vi*) $\frac{1}{90} \times \frac{26{\cdot}80 - 11{\cdot}83}{11{\cdot}83} = K'$ $\therefore K' = {\cdot}01406$

The values of K' obtained are constant within the limits of experimental error, therefore the reaction is of the second order.

30. Trimolecular Reactions. In a trimolecular reaction,

$$A + B + C \longrightarrow D + \ldots\ldots,$$

if a represents the initial concentration of all the three reactants and if x is the proportion of each transformed in t minutes, then the rate of reaction, $\frac{dx}{dt}$, just afte the expiry of t minutes will be represented by the equation

$$\frac{dx}{dt} = K(a - x)^3 \qquad \ldots \qquad (8)$$

This is a differential equation which on integration gives

$$K = \frac{1}{t} \times \frac{x(2a - x)}{2a^2(a - x)^2} \qquad \ldots \qquad (9)$$

In a trimolecular reaction, the time required for the completion of the same fraction of the change is inversely proportional to the square of the initial concentration.

Example 7. *The oxidation of ferrous chloride by potassium chlorate and hydrochloric acid, in aqueous solution, was studied by Noyes and Wason. The reactants were taken in equivalent quantities and the progress of the reaction was followed by titration against standard $KMnO_4$ after adding to the reaction mixture manganous sulphate, sodium phosphate and sulphuric acid. The results obtained are given below :—*

t = Time in minutes	0	1	2	4	15	25
c.c. of $KMnO_4$ required for 25 c.c. of the mixture	49·44	47·50	45·7	42·7	32·83	28·15

Show that the reaction is of the third order.

SOLUTION :—

a in terms of $KMnO_4$ used = 49·44 c.c.

$(a - x)$,, ,, ,, = Values given against each time

First value of K $= \dfrac{1·94(98·88 - 1·94)}{2(49·44)^2 \times (47·5)^2} = ·0000178$

Second value of K $= \dfrac{1}{2} \times \dfrac{3·74(98·88 - 3·74)}{2(49·44)^2 \times (45·7)^2} = ·0000175$

Third value of K $= \dfrac{1}{4} \times \dfrac{6·74(98·88 - 6·74)}{2(49·44)^2 \times (42·7)^2} = ·0000174$

Fourth value of $K = \dfrac{1}{15} \times \dfrac{16·61(98·88 - 16·61)}{2(49·44)^2 \times (32·83)^2} = ·0000173$

Fifth value of K $= \dfrac{1}{25} \times \dfrac{21·29(98·88 - 21·29)}{2(49·44)^2 \times (28·15)^2} = ·0000170$

The values of K obtained are practically constant. Hence the reaction is trimolecular.

EXERCISES

1. Find the order of the reaction

$$2CO \longrightarrow CO_2 + C$$

at 13°C, given that in one experiment the partial pressure of carbon monoxide dropped from 786·8 mm. of mercury to 693 mm. in 30 minutes, and that in a second experiment it dropped from 535·3 mm. to 468·1 m.m. in the same time. (*Chem. Hons. Finals.*)

2. What is meant by the "order of a reaction"? Describe in detail a method of determining the order of reaction. The data for the conversion of a compound A into its isomeride B are as followes:—

Time t =	0	1	2	3	4	6	8
Amount of A : $(a - x)$	49·3	35·6	25·75	18·5	13·8	7·3	4·8

Show that the reaction is of the first order and deduce the formula that you employ. (*B.A., Bombay.*)

3. The spontaneous change of radium emanation, freshly drawn, is a monomolecular reaction. The results obtained were—

Time.	*Volume.*
0	0·102
7	0·062
11	0·044
14	0·033
16·5	0·025
20	0·019
25	0·016
36	0·007
45	0·003
64	0·002
75	0·000

Show how these figures fit the order of reaction.
(*London Hons., Intl.* 1907.)

4. In an investigation of the reaction between hydrogen peroxide and hydriodic acid the following results were obtained:—

Experiment I..Concentration of HI, 0·02; of H_2O_2, 0·02
„ *II* „ „ „ 0·01; „ „ 0·01
„ *III* „ „ „ 0·005; „ „ 0·005

The times taken for the completion of one fourth of the reaction were respectively: 21·7, 43·2, and 97·4 minutes. What is the order of the reaction? (*B.Sc. Hons., Manc.*)

5. Arsine decomposes under the influence of heat into solid arsenic and hydrogen. In an experiment the following results were obtained :—

t (time in hours)	0	5·5	6·5	8
p (pressure in mm. of Hg)	733·32	805·78	818·11	835·34

Calculate the order of reaction and the time required for half the change.

6. Ethyl bromacetate is decomposed by sodium thiosulphate according to the equation

$$C_2H_5.OOC.CH_2Br + Na_2S_2O_3 \rightleftharpoons C_2H_5OOC.CH_2NaS_2O_3 + NaBr$$

The progress of the reaction can be followed by titrating the unchanged thiosulphate against standard iodine solution. 50 c.c. of the reaction mixture required the following amounts of 0·0110 *N* iodine at the times from the commencement of the reaction shown in the table.

t (*min.*) ...	0	5	10	15	25	40	∞
c.c. of I_2 used	37·3	24·7	18·8	15·3	11·6	8·6	4.4

Show that the reaction is of the second order and find the velocity constant for concentrations of 1 mol per litre.

7. The concentrations of a compound undergoing complete change were 5·72, 3·23, 1·96, at the times, 10, 30, and 60 hours from the commencement of the reaction. Ascertain the apparent order of the reaction,

the probable initial concentration, and the velocity constant. (*Hons., Manc.*, 1911.)

8. The rate of reaction between iodine and potassium phenyl propiolate in equivalent quantities was determined (James and Sudborough, J.C.S., 1907) by measuring the rate of disappearance of the iodine. 25 c.c. of the solution was withdrawn after suitable intervals from the reaction mixture and titrated with N/10 sodium thiosulphate.

Times in hours.	*Titration.*
0	24·96
20	10·39
24	9·25
28	8·45
42	6·36

What is the order of reaction, and what is the velocity constant ?

9. In the reaction between equivalent quantities of potassium persulphate and hydrogen peroxide the rate of disappearance of the hydrogen peroxide was measured (Friend, J.C.S., 1906). The numbers given below represent c.c. of N/50 potassium permanganate equivalent to the peroxide remaining in solution. What is the order of the reaction ?

Time in hours.	*c.c. of permanganate.*
0	14·06
1	13·19
2·5	12·05
3·5	11·35
5	10·36
7	9·16

10. Potassium persulphate and potassium iodide interact with the liberation of iodine. 25 c.c. of a solution which was N/30 with respect to both the persulphate and the iodide, were titrated from time to time with N/100 sodium thiosulphate. From the following results

show that the reaction is bimolecular, t being the time of titration and x the number of c.c. of thiosulphate used.

t	9	16	32	50
x	4·52	7·80	14·19	20·05

(*Inst. Chem. Phys., June*, 1909.)

11. Noyes studied the reaction between ferric chloride and stannous chloride by taking equal initial concentrations of both the reactants. The progress of the reaction was followed by titrating a definite volume of the reaction mixture against standard $KMnO_4$, after decomposing the unchanged $SnCl_2$ by mercuric chloride. The results obtained in an experiment are given below:—

t (time in minutes) ...	1	7	17	25	∞
x (c.c. of $KMnO_4$) ...	14·34	36·12	45·02	47·92	62·5

Show that the reaction is trimolecular.

ANSWERS

1. Monomolecular.

3. $\frac{1}{t}\log\frac{Co}{Ct} = 0{\cdot}0309,\ 0{\cdot}0332,\ 0{\cdot}0350,$ 0·0370, 0·0365, 0·0322, 0·0323, 0·0340, 0·0267. **4.** Second.

5. Monomolecular; 19·8 hours. **6.** 14·6.

7. Second order; Initial concentration (mean) = 9·26 Velocity constant (mean) = 0·00670.

8. Second ; $2{\cdot}81\times10^{-3}$, $2{\cdot}83\times10^{-3}$, $2{\cdot}80\times10^{-3}$ $2{\cdot}79\times10^{-3}$. **9.** First. **10.** 0·000255, 0·000259, 0·000253.

CHAPTER VI

DISTRIBUTION LAW

31. Equilibrium in Heterogeneous Systems. A *heterogeneous system* is one which consists of two or more homogeneous parts separated from one another by bounding surfaces. These parts of a heterogeneous system are termed *phases*. Liquid water in equilibrium with its vapour and a saturated solution in contact with an excess of the solute are examples of heterogeneous systems in equilibrium.

Equilibrium in heterogeneous systems, as far as the quantitative compositions of the phases is concerned, is governed by the **distribution law** or **partition law**, which may be stated as follows :—

In a heterogeneous system, at constant temperature, there exists for each molecular species a constant distribution ratio between two phases in contact with each other.

If C_1 and C_2 represent the concentrations of the substance in the two phases, we have :—

$$\frac{C_1}{C_2} = K$$

K is called the **distribution coefficient** or **partition coefficient**, and is independent of the presence of other molecular species and of any chemical reaction that may take place between the different molecular species present.

32. Distribution of a Solute between two Immiscible Liquids. If we shake up a substance with two immiscible or partially miscible solvents, say iodine with water and carbon disulphide, it will distribute itself

between the two solvents. An equilibrium exists between the solute molecules present in the two phases, and, at a given temperature, the ratio between the concentrations of the solute in the two liquids is constant, which is independent of the quantity of solute present. If we add more of the solute to the system, both the concentrations will increase proportionately. Hence the ratio C_1/C_2 will again be the same as before.

The following are a few typical examples of the distribution of a solute between two immiscible solvents, where the molecular weight is the *same* in both the solvents.

Example 1. *At* 15°C *an aqueous solution of succinic acid, containing* 0·070 *gm. in* 10 *c.c., is in equilibrium with an ethereal solution containing* 0·013 *gm. in* 10 *c.c. Succinic acid has its normal molecular weight in both water and ether. What is the concentration of an ethereal solution which is in equilibrium with an aqueous solution containing* 0·024 *gm. in* 10 *c.c.? Calculate also the partition coefficient of succinic acid between water and ether.* (*Punjab B.Sc.*, 1922.)

Concentration of succinic acid in aqueous layer
$= 0{\cdot}070$ gm. per 10 c.c.

Concentration of the acid in ethereal layer
$= 0{\cdot}013$ gm. per 10 c.c.

$\therefore$ Partition Coefficient of succinic acid between water and ether $= \frac{0{\cdot}070}{0{\cdot}013}$ or **5·4.**

Concentration of the ethereal solution in equilibrium with an aqueous solution containing 0·024 gm. in 10 c.c.

$$= 0{\cdot}024 \times \frac{1}{5{\cdot}4} = \mathbf{0{\cdot}0044\ gm.\ per\ 10\ c.c.}$$

Example 2. 0·83 *gm. of succinic acid was shaken up with a mixture of* 100 *c.c. each of water and ether. On analysis the aqueous layer was found to contain* 0·70 *gm. of the acid. Calculate the quantity of succinic acid*

that can be extracted from a litre of an ethereal solution containing 1·00 *gm. of the acid by shaking it* (1) *with* 100 *c.c. of water, and* (2) *with two successive quantities,* 50. *c.c. each, of water.*

Concentration of succinic acid in the aqueous layer
$= 0{\cdot}70$ gm. per 100 c.c.

Concentration of the acid in the ethereal layer
$= 0{\cdot}83 - 0{\cdot}70$ or $0{\cdot}13$ gm. per 100 c.c.

$\therefore$ Partition coefficient of succinic acid between water and ether $= \frac{0{\cdot}70}{0{\cdot}13}$ or $5{\cdot}4$.

(1) Let x gm. be the quantity of succinic acid extracted by 100 c.c of water from a litre of the ethereal solution containing 1·00 gm. per litre. The concentration of the acid in the aqueous layer is, therefore, x gm. per 100 c.c. and that in the ethereal layer $\frac{1-x}{10}$ gm. per 100 c.c.

From the Partition Law we have:—

$$\frac{x}{\frac{1-x}{10}} = 5{\cdot}4; \text{ whence } x = 0{\cdot}35.$$

Hence the quantity of succinic acid that can be extracted from a litre of an ethereal solution containing 1·00 gm. of the acid by shaking it with 100 c.c. of water $= \mathbf{0{\cdot}35}$ **gm.**

(2) Let x_1 be the quantity of succinic acid extracted by the first 50 c.c. of water. The concentration of the acid in the aqueous layer is therefore $2x_1$ gm. per 100 c.c. and that in the ethereal layer $\frac{1-x_1}{10}$ gm. per 100 c.c.

$$\therefore \frac{2x_1}{\frac{1-x_1}{10}} = 5{\cdot}4; \text{ or, } x_1 = 0{\cdot}21.$$

After the first extraction the quantity of succinic acid in the ethereal layer is $1-,0{\cdot}21$ or $0{\cdot}79$ gm. If x_2 is

the quantity of succinic acid extracted by the second 50 c.c. of water, the concentration of the acid in the aqueous layer is $2x_2$ gm. per 100 c.c. and that in the ethereal layer $\frac{0{\cdot}79 - x_2}{10}$ gm.

$$\therefore \frac{2x_2}{\frac{0{\cdot}79 - x_2}{10}} = 5{\cdot}4 \text{ ; whence } x_2 = 0{\cdot}19.$$

Hence the total quantity of succinic acid extracted
$= 0{\cdot}21 + 0{\cdot}19$ or **0·40 gm.**

Example 3. *The partition coefficient of iodine for water and carbon disulphide is* 0·0017. *What quantity of iodine can be extracted by shaking a litre of an aqueous solution containing* 1·00 *gm. of iodine with four successive quantities of* 10 *c.c. each of carbon disulphide.*

Let x_1 gm. be the quantity of iodine extracted by the first 10 c.c. of carbon disulphide. The concentration of iodine in the carbon disulphide layer is, therefore, $100\,x_1$ gm. per litre, while in the aqueous layer it is $1{\cdot}00 - x_1$ gm. per litre.

From the Distribution Law we have:—

$$\frac{1{\cdot}00 - x_1}{100x_1} = 0{\cdot}0017$$

Whence, $$x_1 = \frac{1{\cdot}00}{1{\cdot}17} \text{ or } 0{\cdot}855.$$

If x_2 is the quantity of iodine extracted by the second 10 c.c. of carbon disulphide, the concentration of iodine in the carbon disulphide layer will be $100x_2$ gm. per litre and that in the aqueous layer $1{\cdot}00 - x_1 - x_2$ gm. per litre.

$$\therefore \frac{1{\cdot}00 - x_1 - x_2}{100\,x_2} = 0{\cdot}0017.$$

Whence, $$x_2 = \frac{1{\cdot}00 - x_1}{1{\cdot}17} = \frac{0{\cdot}145}{1{\cdot}17} = 0{\cdot}124.$$

Similarly, $x_3 = \dfrac{1 - x_1 - x_2}{1{\cdot}17} = 0{\cdot}0179$;

and $x_4 = \dfrac{1 - x_1 - x_2 - x_3}{1{\cdot}17} = 0{\cdot}00265.$

Total quantity of iodine extracted $\therefore$

$= 0{\cdot}855 + 0{\cdot}124 + 0{\cdot}0179 + 0{\cdot}00265 = \mathbf{1{\cdot}00}.$

Hence the extraction is complete.

33. Association in Solution. In liquid liquid systems the solute may sometimes have different molecular weights in the two solvents. Let us suppose that it has its normal molecular weight in one of the solvents, whilst in the other it is more or less completely associated to form complex molecules according to the equation :—

$$nX \rightleftharpoons Xn$$

Let the concentration of the solute in the first solvent, in which all the molecules are simple, be C_1 and that in the second solvent, where more or less complete association has occurred, be C_2 (see Fig. 1). Further, let α represent the degree of dissociation of the associated molecules in the second solvent.

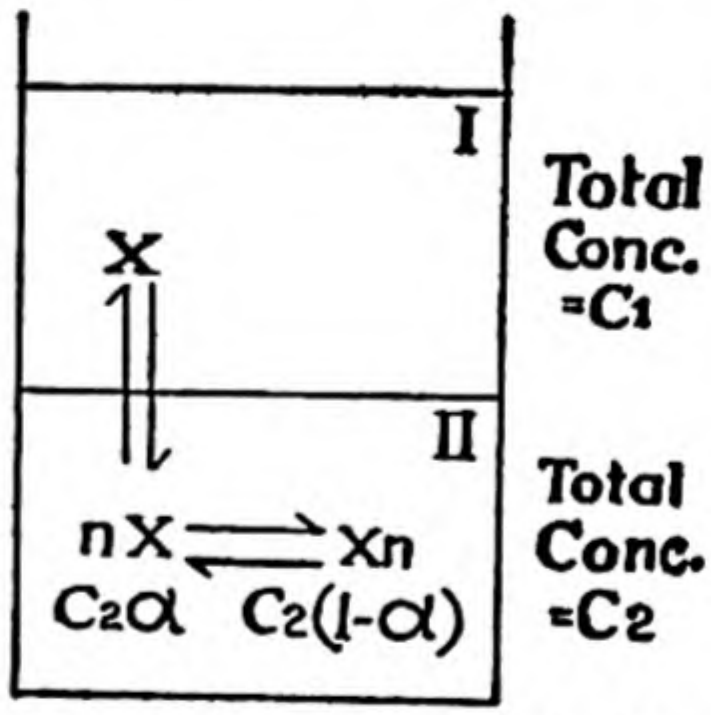


Fig. 1. Distribution Diagram for an Associated Solute.

By applying Mass Action Law we have :

$$\frac{(C_2\alpha)^n}{C_2(1-\alpha)} = K.$$

Hence $C_2\alpha$, the concentration of simple molecules in phase II, is equal to

$$\sqrt[n]{C_2(1-\alpha)K}.$$

Inserting this value in the distribution formula, we have :

$$K_1 = \frac{C_1}{C_2\alpha} = \frac{C_1}{\sqrt[n]{C_2(1-\alpha)K}}$$

$$\text{or, } \frac{C_1}{\sqrt[n]{C_2(1-\alpha)}} = K_2$$

Since in most cases association is practically complete, *i.e.* α is negligibly small, the above expression assumes the simplified form,

$$\frac{C_1}{\sqrt[n]{C_2}} = \text{constant},$$

which may be used for finding the degree of complexity of the associated molecules with respect to the simple molecules. A number of determinations are made of the values of C_1 and C_2 using different quantities of the solute or the solvents. The value of n, which gives the nearest approach to constancy in the above formula, is taken as the degree of complexity of the associated molecules.

Example 4. *Succinic acid has its normal molecular weight in water. In the distribution of the acid between water and benzene the concentrations in the water and benzene layers were found to be C_1 and C_2 respectively.*

C_1	0·150	0·195	0·289 gm. per 100 c.c.
C_2	2·420	4·120	9·700 „ „

Calculate the molecular weight of succinic acid in benzene.

The distribution of a solute between two solvents, in one of which it has its normal molecular weight while in the other it exists in the form of associated molecules, is given by the formula :

$$\frac{C_1}{\sqrt[n]{C_2}} = K$$

Putting $n = 1$, we have :

$$\frac{C_1}{C_2} = \frac{0{\cdot}150}{2{\cdot}420} \text{ or } 0{\cdot}062$$

$$= \frac{0{\cdot}195}{4{\cdot}120} \text{ or } 0{\cdot}047$$

$$= \frac{0{\cdot}289}{9{\cdot}700} \text{or } 0{\cdot}030.$$

Since the value of C_1/C_2 is not constant, the molecular weight of succinic acid in benzene is not normal.

Putting $n = 2$, we have :

$$\frac{C_1}{\sqrt{C_2}} = \frac{0{\cdot}150}{\sqrt{2{\cdot}420}} \text{ or } 0{\cdot}096$$

$$= \frac{0{\cdot}195}{\sqrt{4{\cdot}120}} \text{or } 0{\cdot}096$$

$$= \frac{0{\cdot}289}{\sqrt{9{\cdot}700}} \text{ or } 0{\cdot}093$$

We see from the above that the value of $C_1/\sqrt{C_2}$ is practically constant. Hence in benzene solution succinic acid, $(CH_2COOH)_2$, exists as double molecules, and its molecular weight is therefore 118×2 or **236.**

34. Distribution of a Substance Undergoing Combination. The following example illustrates the application of the partition law to a substance undergoing combination in one of the phases.

Example 5. *A solution of potassium iodide containing* 7·92 *gm. of the salt per litre was thoroughly shaken with iodine and carbon disulphide. On analyzing the aqueous and the carbon disulphide layers, the former was found to contain* 2·13 *gm. of iodine and the latter* 35·67 *gm. Calculate the dissociation constant of the tri-iodide formed in aqueous solution according to the equation:—*

$$KI + I_2 \rightleftharpoons KI_3,$$

assuming KI and KI_3 to be insoluble in carbon disulphide.

The distribution coefficient of iodine for carbon disulphide and water is 410.

The distribution of iodine between water and carbon disulphide is shown in Fig. 2.

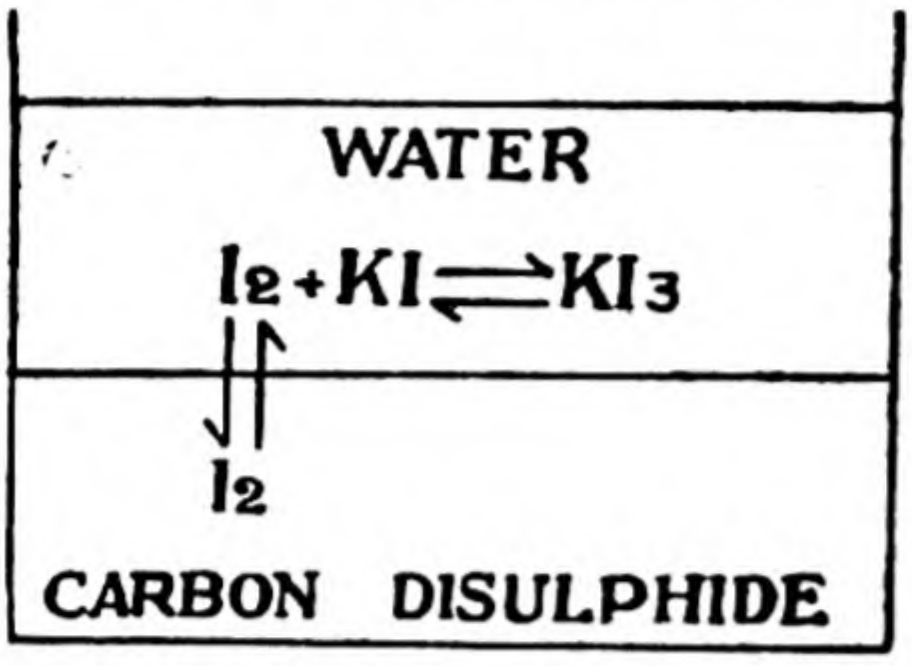


Fig. 2. Distribution of Iodine between CS_2 and H_2O.

The equilibrium in the aqueous layer is governed by the law of mass action, and the dissociation constant of the tri-iodide is given by the equation

$$\frac{[I_2] \times [KI]}{[KI_3]} = K.$$

By Partition Law, the concentration of *free* iodine in the aqueous layer

$$= \frac{\text{Concentration of Iodine in } CS_2}{410}$$

$$= \frac{35{\cdot}67}{410} \text{ or } 0{\cdot}0870 \text{ gm. per litre}$$

$$= \frac{0{\cdot}0870}{127 \times 2} \text{ or } 0{\cdot}000343 \text{ mols per litre.}$$

$$\therefore [I_2] = 0{\cdot}000343.$$

Amount of iodine per litre of the aqueous solution that has combined with KI $= 2{\cdot}13 - 0{\cdot}087$ or $2{\cdot}043$ gm.

Hence the concentration of $KI_3 = 2{\cdot}043 \times \frac{420}{254}$ gm. per litre

$$= 2{\cdot}043 \times \frac{420}{254} \times \frac{1}{420} \text{ or } 0{\cdot}00804 \text{ mols per litre.}$$

$$\therefore [KI_3] = 0{\cdot}00804.$$

The original concentration of KI in mols per litre

$$= \frac{7{\cdot}92}{166} \text{ or } 0{\cdot}0477.$$

Decrease in the molar concentration of KI due to the formation of $KI_3 = 0{\cdot}00804$.

∴ The equilibrium concentration of KI in mols per litre, *i.e.*, [KI], is equal to 0·0477 − 0·00804 or 0·0397.

Substituting the values of $[I_2]$, $[KI_3]$, and [KI] in the mass-law equation, we get the dissociation constant,

$$K = \frac{0{\cdot}000343 \times 0{\cdot}0397}{0{\cdot}00804} = \mathbf{0{\cdot}00169.}$$

35. Solubility of Gases in Liquids. A gas in contact with its saturated solution constitutes a system in heterogeneous equilibrium, governed by the Distribution Law. The concentration C_1 of the gas in the liquid phase, *i.e.* its *solubility*, should bear a constant ratio to the concentration C_2 of the gas in the gaseous phase, *i.e.*, its *density*. Now, density is proportional to the pressure of the gas. Hence, we conclude:

The solubility of a gas in a liquid at a given temperature is proportional to the pressure of the gas.

This generalization, which, as we have seen, is a particular case of Distribution Law, was first discovered experimentally by Henry in 1803, and is known as **Henry's law.** The distribution co-efficient C_1/C_2 in this case is termed the **coefficient of solubility.**

In the case of a *gaseous mixture*, laws of Henry and Dalton both apply, and the solubility of each constituent is proportional to its partial pressure.

Henry's law may be more simply stated by expressing the solubility in terms of the *volume* of the gas dissolved, instead of its weight. We know that the effect of increasing the pressure on the system is twofold: (*i*) proportionate increase of solubility (Henry's law), (*ii*) proportionate decrease of volume (Boyle's law). Suppose x gm. of the gas, occupying v units of volume, are dissolved by a unit volume of the liquid, when the pressure on the system is P. If, now, the pressure be increased to nP the amount of the gas dissolved will be nx gm. (Henry's law). This quantity of the gas would occupy, under the original pressure P a volume equal to nv. But nx gm. of the gas under the new pressure nP would occupy only $1/n$th of

this volume, *i*.e., nv/n or v units (Boyle's law). Hence, *volume of a gas dissolved by a unit volume of a liquid at a given temperature is constant, whatever the pressure on the gas.*

The volume of a gas dissolved by a unit volume of a liquid is the *coefficient of solubility* of the gas at the given temperature.

Example 6. *The solubility coefficients of oxygen and nitrogen in water at* 0°*C are respectively* 0·04 *and* 0·02. *Calculate the volumetric composition of the gas expelled on boiling the water which has been saturated by free exposure to air at* 0°*C, assuming the composition of air by volume to be* 21 *per cent. oxygen and* 79 *per cent. nitrogen.*

Partial pressure of oxygen in the air $= \frac{21}{100}$ atmos.

Partial pressure of nitrogen in the air $= \frac{79}{100}$ atmos.

Volume of oxygen measured at the atmospheric pressure, dissolved by 1 volume of water at 0°C and under 1 atmosphere pressure = 0·04.

∴ Volume of oxygen, measured at the atmospheric pressure, dissolved by 1 volume of water at 0°C and under a pressure of 21/100 atmos.

$$= 0{\cdot}04 \times \frac{21}{100} \text{ or } 0{\cdot}0084.$$

Similarly, volume of nitrogen, measured at the atmospheric pressure, dissolved by 1 volume of water at 0°C and under a pressure of 79/100 atmos.

$$= 0{\cdot}02 \times \frac{79}{100} \text{ or } 0{\cdot}0158.$$

Total volume of gas, measured at the atmospheric-pressure, dissolved by 1 volume of water at 0°C

$= 0{\cdot}$~~0084~~ 0·0158 or 0·0242.

·0084 + 0·0158 or 0·0242.

∴ Percentage composition by volume of the gas expelled by boiling the solution is as follows :—

$$O_2 = \frac{0{\cdot}0084}{0{\cdot}0242} \times 100 \text{ or } \mathbf{34{\cdot}7 \text{ per cent.}}$$

$$N_2 = \frac{0{\cdot}0158}{0{\cdot}0242} \times 100 \text{ or } \mathbf{65{\cdot}3 \text{ per cent.}}$$

Example 7. *One litre of air-free water is shaken in a closed space with two litres of oxygen at 0°C and an initial pressure of 760 mm. Calculate (a) the pressure of the gas at equilibrium, and (b) the volume of the gas measured at N.T.P. that has been absorbed. The solubility coefficient of oxygen at 0°C is* 0·04.

(*a*) Let P mm. be the pressure of the gas at equilibrium. Two litres of the gas measured at $(760 - P)$ mm., pressure have been absorbed by the water. This amount now occupies a volume of 1 litre, *i.e.*, the volume occupied by the solution (see Fig. 3). Hence it would exert a pressure of $2 \times (760 - P)$ mm.

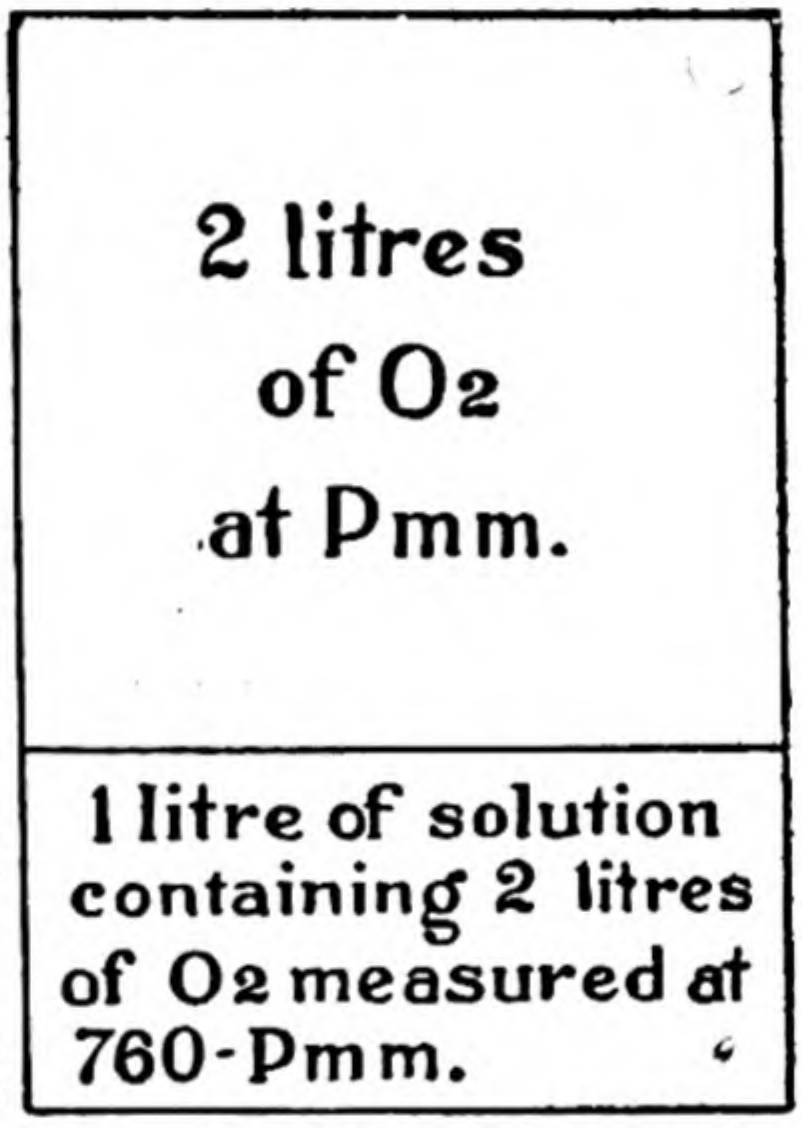


Fig. 3. Distribution diagram of the gas, representing the state of things at equilibrium

From the Distribution Law we have :

$$\frac{\text{Concentration of gas in solution}}{\text{Concentration of gas in gaseous phase}} = 0{\cdot}04.$$

Or, since the concentrations are proportional to pressures,

$$\frac{2 \times (760 - P)}{P} = 0{\cdot}04 ;$$

whence, $P = \mathbf{745 \text{ mm.}}$

(*b*) The volume of the gas that has been absorbed measured at 0°C and a pressure of 760 − 745 mm., or 15 mm

is 2 litres. When measured at 0°C and 760 mm. pressure, this volume would become

$$2 \times \frac{15}{760} \text{ or } \mathbf{0{\cdot}0395 \text{ litre.}}$$

Example 8. *One litre of a mixture of oxygen and carbon dioxide in equal proportions by volume is shaken with* 1 *litre of water at* 0°*C until equilibrium is established. The initial pressure is* 760 *mm. Calculate the final pressure and the composition of the residual gas. (The coefficients of absorption at* 0° *are:* O_2, 0·04; CO_2, 1·8.)
(*Inst. Chem. Inter. July* 1906.)

Initial pressure of $O_2 = 380$ mm.

Initial pressure of $CO_2 = 380$ mm.

Let the equilibrium pressures of O_2 and CO_2 in the gaseous phase be P_1 and P_2 respectively. The pressure of dissolved oxygen will be $(380 - P_1)$ mm. and that of carbon dioxide $(380 - P_2)$ mm.

By Distribution Law we have :

$$\frac{380 - P_1}{P_1} = 0{\cdot}04 \text{ ; whence } P_1 = 365 \text{ mm.}$$

and

$$\frac{380 - P_2}{P_2} = 1{\cdot}8 \text{; whence } P_2 = 136 \text{ mm.}$$

Hence, the total pressure of the gas at equilibrium $= 365 + 136$ or **501 mm.**

Composition of the residual gas will be :

$$O_2 = \frac{365}{501} \times 100, \text{ or } \mathbf{72{\cdot}9\%}$$

$$CO_2 = \frac{136}{501} \times 100, \text{ or } \mathbf{27{\cdot}1\%}$$

Example 9. **3** *litres of a mixture of oxygen* (1 *vol.*) *and nitrogen* (2 *vol.*) *at* 0°*C and an initial pressure of* 1 *atmosphere are shaken in a closed space with a litre of water at the same temperature. Calculate the percentage composition of the gas that can be obtained by boiling the*

solution, and the partial pressures P_1 *and* P_2 *of oxygen and nitrogen at equilibrium.* (*solubility coefficients of* O_2 *and* N_2 *are* 0·04 *and* 0·02 *respectively*).

Initial pressure of $O_2 = \frac{1}{3}$ atmos.

Initial pressure of $N_2 = \frac{2}{3}$ atmos.

Three litres of oxygen measured at 0°C and $(\frac{1}{3} - P_1)$ atmosphere pressure have been absorbed by the water. This amount of the gas now occupies a volume of 1 litre, *i.e* the volume occupied by the solution. Hence it would exert a pressure of $3(\frac{1}{3} - P_1)$ or $1 - 3\ P_1$ atmosphere.

From the Partition Law we have:

$$\frac{1 - 3P_1}{P_1} = 0{\cdot}04.$$

Whence, $P_1 = \mathbf{0{\cdot}33}$ **atmos.**

Similarly, the final partial pressure P_2 of nitrogen is given by the equation

$$\frac{2 - 3P_2}{P_2} = 0{\cdot}02$$

Whence, $P_2 = \mathbf{0{\cdot}66}$ **atmos.**

The volume of oxygen that has been absorbed, measured at 0°C and 0·33 atmosphere pressure, is 0·04 litre. At 1 atmosphere pressure this volume would become 0·04 × 0·33 or 0·0132 litre.

Similarly, the volume of nitrogen that has been absorbed, measured at 1 atmosphere pressure, is 0·02 × 0·66 or 0·0132 litre.

Hence the percentage composition of the gas that can be obtained by boiling the solution is:

$$\mathbf{O_2 = 50\%}$$
$$\mathbf{N_2 = 50\%}$$

Example 10. ***A natural water, on being boiled gave a mixture of gases having the following volumetric***

composition : O_2, 21·0°/₀ ; N_2, 39·4°/₀ ; CO_2, 39·6°/₀. *What was the composition of the air with which the water had been in contact? The solubility coefficients of the three gases are* 0·04, 0·02, *and* 1·8 *respectively.*

Let the partial pressures of O_2, N_2, and CO_2 in the air with which the water had been in contact be P_1, P_2, and P_3 respectively.

Partial pressures of dissolved gases were :

$$O_2 = 21{\cdot}0\%$$
$$N_2 = 39{\cdot}4\%$$
$$CO_2 = 39{\cdot}6\%$$

From the Distribution Law we have :

$$\frac{21{\cdot}0}{P_1} = 0{\cdot}04;\ \text{whence, } P_1 = 525.$$

$$\frac{39{\cdot}4}{P_2} = 0{\cdot}02;\ \text{whence, } P_2 = 1970;$$

$$\text{and } \frac{39{\cdot}6}{P_3} = 1{\cdot}8;\ \text{whence, } P_3 = 22$$

$$\therefore\ P_1 + P_2 + P_3 = 525 + 1970 + 22 = 2517$$

Hence, the composition of the air with which the water had been in contact was :

$$O_2 = \frac{525}{2517} \times 100 \text{ or } \mathbf{20{\cdot}8}\ \%$$

$$N_2 = \frac{1970}{2517} \times 100 \text{ or } \mathbf{78{\cdot}3}\%$$

$$CO_2 = \frac{22}{2517} \times 100 \text{ or } \mathbf{0{\cdot}9}\%.$$

PROBLEMS

1. Nernst studied the distribution of succinic acid between water and ether, and obtained the following results :—

	(*i*)	(*ii*)	(*iii*)
C_1 ...	0·24	0·70	1·21
C_2 ...	0·046	0·13	0·22

C_1 and C_2 represent the concentrations in grams per 100 c.c. respectively of water and ether. Show that these results illustrate the Law of Distribution.

2. The distribution-coefficient of iodine for carbon tetrachloride and water at 25°C is 85·5. The solubility of iodine in water at 25°C is 0·340 gram per litre. Calculate the solubility of iodine in carbon tetrachloride at 25°, assuming complete non miscibility between the two solvents.

3. The partition-coefficient of iodine for CCl_4/water is 85·5. What weight of iodine can be extracted by shaking a litre of an aqueous solution containing one gram of iodine with four successive quantities of 10 c.c. each of carbon tetrachloride? How much of iodine would have been extracted if the whole of the carbon tetrachloride had been used at once?

4. An aqueous solution of succinic acid containing 7·0 grams per litre is in equilibrium with an ethereal solution containing 1·3 grams per litre. Calculate the concentration of the aqueous solution which is in equilibrium with an ethereal solution containing 2·0 grams of the acid per litre.

5. The distribution of benzoic acid between water and benzene was studied by shaking different amounts of the acid with the two solvents. Each time, 10 c.c. of the aqueous and the benzene layers were withdrawn and titrated against the same alkali solution. The results obtained are tabulated below:—

Alkali required for 10 c.c. of aqueous solution.	*Alkali required for 10 c.c. of benzene solution.*
2·55 c.c.	9·75 c.c.
3·55 c.c.	18·50 c.c.
5·30 c.c.	43·00 c.c.

Calculate the partition coefficient of benzoic acid between water and benzene, and also the degree of complexity of its molecules in the benzene solution as compared with that in the aqueous solution.

6. Experiments on the ratio of distribution of phenol between water and chloroform gave the followiug numbers :

Aqueous solution.	*Chloroform solution.*
0·074	0·254
0·163	0·761
0·247	1·85
0·436	5·43

What conclusions may be drawn from these results regarding the molecular condition of phenol in chloroform solution? (*Downing College, Cambridge.*)

7. Beckmann studied the distribution of thiophene between liquid benzene and solid benzene. The concentrations of the substance in the liquid phase C_1 and that in the solid phase, C_2, expressed in grams of thiophene per 100 grams of benzene are given below :

C_1	...	1·22	4·50	6·44
C_2	...	0·48	1·87	2·66

What is the molecular condition of thiophene in solid benzene with respect to that in liquid benzene.

8. A benzene solution of ethyl acetate containing 50 gm./l. is shaken at 12°C with half its volume of distilled water until equilibrium is established. Given that the partition coefficient between benzene and water is 10·7 at 12°, what difference should be found between the freezing point of the aqueous layer and that of distilled water? Molecular depression constant for water = 18·6° referred to 100 gm. (*London B.Sc. Hons.*, 1922.)

9. A saturated solution of iodine in water at 25°C contains 0·34 gm. per litre. The partition coefficient of iodine between a given solvent and water is 85·5. What will be the weight of iodine per litre contained in the solvent when it is in equilibrium with the saturated aqueous solution? (*Inter. Sci. Sheffield.*)

10. If the volume of an aqueous solutions of benzoic acid of known strength be one litre, and that of the ether added each time be 200 c.c., find the quantity of the acid which will be left in the water at the end of the third extraction. The partition coefficient of benzoic acid between water and ether is 1/80. (*Punjab B.Sc.* 1923.)

11. A solution of oxalic acid containing 22·35 gm. $(COOH)_2$ per litre at 11°C is shaken with an equal volume of ether at the same temperature. 10 c.c. of the aqueous layer required 45·10 c.c. of N/10 $KMnO_4$. Calculate the partition coefficient of oxalic acid between water and ether at 11°C.

12. Acetic acid has its normal molecular weight in water. In the distribution of the acid between water and carbon tetrachloride, the molar concentrations in the water and carbon tetrachloride layers were found to be C_1 and C_2 respectively.

C_1	0·292	0·363	0·725	1·41
C_2	4·87	5·42	7·98	10·7

Calculate the molecular weight of acetic acid in carbon tetrachloride.

13. A litre of carbon dioxide at 10°C and an initial pressure of one atmosphere is shaken in a closed vessel with four litres of air-free water at the same temperature. Calculate the weight of carbon dioxide dissolved, and the final pressure of the gas when the absorption is complete. The absorption-coefficient of carbon dioxide at 10°C is 1·18.

14. Air containing 29·9% oxygen, 79·0% nitrogen and 0·1% CO_2 is shaken with half its volume of air-free water at 0°C in a closed vessel. The initial pressure of air was 1 atmosphere. Calculate (1) the equilibrium partial pressures p_1, p_2 and p_3 of the three constituents of the unabsorbed gas, and (2) the composition of the gaseous mixture which can be obtained on boiling the solution? The coefficients of solubility at 0°C of O_2, N_2 and CO_2 are 0·04, 0·02 and 1·8 respectively.

ANSWERS

2. 29·1 gm. per litre.

3. 0·915; 0·774. **4.** 10·8 gm. per litre.

5. 1·15; double molecules in benzene.

6. $(C_6H_5OH)_2$ in concentrated solution.

7. Same molecular condition.

8. 0·093°C **9.** 29·1 gm. per litre.

10. 0·0002 gm. **11.** 9·9.

12. 120. **13.** 1·65 gm.; 0·171 atoms.

14. (1) 0·205; 0·782; 0·000526.

(2) $O_2 = 33{\cdot}1\%$, $N_2 = 63{\cdot}1\%$, $CO_2 = 3{\cdot}8\%$.

CHAPTER VII

THERMOCHEMISTRY

36. Exothermic and Endothermic Reactions. Thermochemistry deals with energy changes that always accompany chemical reactions. A reaction attended by the liberation of energy is called *exothermic*, while the one that proceeds with absorption of energy is termed *endothermic*. The amount of energy evolved or absorbed during a chemical change is the same for the same quantities of the reacting substances. The energy given out during a chemical change generally appears in the form of heat, while that which is absorbed may be in the form of thermal, electrical, or photo-energy.

37. Thermochemical Units. The units adopted in thermo-chemical measurements are :—

1. The **calorie** (cal.), "gram-calorie", or the "small" calorie. This represents the quantity of heat required to raise the temperature of 1 gram of water through 1°C (15° to 16°C), and is written with a *small* c.

2. The **Calorie** (Cal.). "killogram calorie", or the "big calorie". This is 1000 times the small calorie, and represents the heat required to raise the temperature of 1 killogram of water through 1°C. It is always written with a *capital* C.

38. Thermochemical Equations. A thermochemical equation represents both the "matter change" and the "energy change" involved in a chemical reaction. Thus,

$$C + O_2 \longrightarrow CO_2 + 97 \text{ Cals.}$$

indicates that when carbon burns in oxygen to form carbon

dioxide, 97 killogramme calories of heat are set free per 1 mol of carbon dioxide produced. Again,

$$C + 2S \longrightarrow CS_2 - 26 \text{ Cals.}$$

means that 26 killogramme calories of heat are *absorbed* (note the *minus* sign) when a mol of CS_2 is produced from its elements.

For the sake of brevity, the above two equations are written as energy equations:—

$$(C, O_2) \longrightarrow +97 \text{ Cals.}$$

$$(C, S_2) \longrightarrow -26 \text{ Cals.}$$

The positive sign always signifies the evolution and the negative sign the absorption of heat during the reaction.

It must be noted that the thermal value of a reaction depends upon the **state of aggregation** and the **temperature** of the substances taking part in the change. When nothing else is specified, it is understood that the substances exist in their normal physical states and at the ordinary temperature.

39. Terminology :—

1. **Heat of Formation.** The quantity of heat evolved or absorbed during the formation of *one mol* of a substance from its elements is called its "heat of formation". Thus, the heat of formation of carbon dioxide is 97 Cals., while that of carbon disulphide is −26 Cals.

A compound produced from its elements with evolution of heat is called an **exothermic compound**, while one produced with absorption of heat is known as an **endothermic compound**. Thus, carbon dioxide is an "exothermic" and carbon disulphide an "endothermic" compound.

2. **Heat of Solution.** The heat given out during the dissolution of 1 mol of a substance in an *excess* of the solvent is termed its "heat of solution". Thus, in the equation,

$$(KCl, Aq) \longrightarrow -4{\cdot}4 \text{ Cals.},$$

−4·4 Cals. represents the heat of solution of KCl. The equation,

$$(H, Cl, Aq) \longrightarrow 39{\cdot}3 \text{ Cals.},$$

represent the heat of formation *plus* the heat of solution of HCl.

3. **Heat of Combustion.** The heat evolved during the complete combustion of 1 mol of a substance is called its " heat of combustion". Thus, "the heat of combustion of methane is 210·8 Cals. :—

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + 210{\cdot}8 \text{ Cals.}$$

4. **Heat of Neutralization.** The heat given out during the complete neutralization of 1 *gram-equivalent* of an acid by a base in *dilute* aqueous solution is termed the "heat of neutralization" of the acid by the base. The heats of neutralization of strong acids by strong bases are practically the same, while in the case of weak acids or weak bases they are different.

40. Energy Equations. Law of Conservation of Energy is the fundamental law of thermochemistry. According to this Law the total amount of energy in an isolated system undergoing a change, physical or chemical, remains the same before and after the change. Thermochemical calculations can be performed in a very simple manner with the help of *energy equations.* In order to do this we must be able to associate with a molecule of each substance a definite amount of **intrinsic energy.** Since we can have no knowledge of the *energy content* or intrinsic energy of an element, or differences between the intrinsic energies of different elements, a simple assumption is made for the sake of convenience that the intrinsic energy of the commonly occuring form of each element is zero. This is far from being true ; but since in thermochemistry we only deal with differences of energy between one chemical system and another, the assumption is very helpful in simplifying thermochemical calculations.

Now suppose that x Cals. of heat are given out during the formation of one mol of a compound AB from its elements A and B.

$$A + B \longrightarrow AB + x \text{ Cals.}$$

Since A and B are elements, the sum of their intrinsic energies must be equal to zero, and, by the law of con-

servation of energy, the sum of the energies on the other side of the equation should also be equal to zero. This will mean that the intrinsic energy of AB will be equal to $-x$ Cals. In other words, *the intrinsic energy of a compound must be equal to its heat of formation with the sign changed.*

Example 1. *Calculate the heat of formation of methane, CH_4, given that*

$$C + O_2 = CO_2 + 96{\cdot}9 \text{ Cals.}$$
$$H_2 + O = H_2O + 68{\cdot}4 \text{ Cals.}$$
$$CH_4 + 4O = CO_2 + 2H_2O + 213{\cdot}5 \text{ Cal.}$$

Is methane an endothermic or exothermic substance? (*Punjab B.Sc.* 1915.)

Let the heat of formation of $CH_4 = x$ Cals.
∴ Its intrinsic energy $= -x$,,
Intrinsic energy of CO_2 $= -96{\cdot}9$ Cals.
,, ,, ,, H_2O $= -68{\cdot}4$,,
Substituting these values in the equation

$$CH_4 + 4O = CO_2 + 2H_2O + 213{\cdot}5 \text{ Cals.}$$

we get

$$-x + 0 = -96{\cdot}9 - 2 \times 68{\cdot}4 + 213{\cdot}5$$

Whence $-x = -20{\cdot}2$ Cals.
or $x = 20{\cdot}2$ Cals.
Since x is positive, CH_4 is an **exothermic** compound.

Example 2. *The heats of combustion of a gram-atom of carbon, a gram-molecule of hydrogen, and a gram-molecule of acetic acid are respectively* 96960, 68160, *and* 209600 *calories. Calculate the heat of formation of a gram molecule of acetic acid.* (*Punjab B.Sc.* 1916.)

Let the heat of formation of acetic acid = x cals.
Then its intrinsic energy $= -x$ cals.
C, O_2 is given = 96960 cals.
H_2, O ,, ,, = 68160 ,,

Hence the intrinsic energy of CO_2 $= -96960$ cals.

and „ „ „ „ „ H_2O $= -68160$ „

Substituting these values in the following energy equation

$$CH_3COOH + 2O_2 = 2CO_2 + 2H_2O + 209600 \text{ cals.}$$

$$-x + 0 = -2 \times 96960 - 2 \times 68160 + 209600$$

Whence $-x = -120640$ cals.

or $x =$ **120640 cals.**

Example 3: *Calculate the heat given out in the preparation of magnesium from magnesium chloride and sodium. The heat of formation of magnesium chloride and of sodium chloride being* 1510 *Cals., and* 1954 *Cals. respectively. State the thermochemical law which underlies your calculation.* (*Allahabad M.A.* 1897.)

Let the heat of preparation of Mg from $MgCl_2$ and Na be x Cals.

Then $MgCl_2 + 2Na = Mg + 2NaCl + x$ Cals.

The intrinsic energy of $MgCl_2 = -1510$ Cals.

and „ „ „ $NaCl = -1954$ „

By substituting these values in the above equation we get

$$-1510 + 0 = 0 - 2 \times 1954 + x$$

Whence x **=2398 Cals.**

The law underlying the calculation is that sum of the intrinsic energies of the reactants is equal to the sum of the intrinsic energies of the resultants and the thermal value of the reaction.

41. Hess's Law of Constant Heat Summation. The law of conservation of energy would lead us to expect that 'the total heat evolved or absorbed during a reaction would be independent of the stages by which the reaction is completed'. This was experimentally shown to be true by Hess in the year 1840, and is called Hess's Law. Thus, if A + B changes into C + D by the following three reactions, then the total thermal value of the change must be

the same, whether it takes place in one stage as in *(i)* or in two stages as in *(ii)* or in three stages as in *(iii)*

$$\begin{aligned}
(i)\quad & A + B = C + D + x \text{ Cals.}\\
(ii)\quad & A + B = E + F + a \text{ Cals.}\\
& E + F = C + D + b \text{ Cals.}\\
(iii)\quad & \tfrac{1}{2}A + B = M + N + c \text{ Cals.}\\
& \tfrac{1}{2}A + M = K + d \text{ Cals.}\\
& K + N = C + D + e \text{ Cals.}
\end{aligned}$$

Then $x = a + b$

and also $= c + d + e$

Hess's Law is very serviceable in determining indirectly the heats of formation and also in otherwise finding out the heats of reactions. Thus, while heats of combustion of both carbon and carbon monoxide can be easily determined by experiment, it is not possible to synthesise carbon monoxide from its elements and to find out its heat of formation. Hess's Law is helpful in finding out this heat of formation by a very simple calculation.

$$C, O_2 = 96{\cdot}96 \text{ Cals.}$$

$$CO, O = 68{\cdot}00 \text{ Cals.}$$

The reaction

$$C + O_2 = CO_2$$

may be supposed to take place in two stages when

$$C + O = CO + x \text{ Cals.}$$

and $CO + O = CO_2 + 68{\cdot}00$ Cals.

$\therefore\ 68{\cdot}00 + x = 96{\cdot}96$

and x, the heat of formation of CO will be equal to

$$96{\cdot}96 - 68{\cdot}00 = 28{\cdot}96 \text{ Cals.}$$

Example 4. *On dissolving* 100 *grams of anhydrous copper sulphate in water the heat evolved amounted to* 9990 *cals, while the same weight of crystallized copper sulphate* ($CuSO_4 . 5H_2O$) *gave an absorption of heat amounting to* 1100 *cals. Determine the heat of trans-*

formation of the gram molecule of $CuSO_4$ *into* $CuSO_4.5H_2O$. (*Punjab B.Sc. Hons.* 1915.)

$CuSO_4 = 63+32+64 = 159$

and $CuSO_4.5H_2O = 159+90 = 249$

When 100 gm. of $CuSO_4$ are dissolved in water the heat evolved $=9990$ cals.

∴ The heat evolved on dissolving 159 gm. (*i.e.*, one mol)

$$= \frac{159}{100} \times 9990 \text{ cals.}$$

On dissolving in water, $CuSO_4$ first gets hydrated, or changed into $CuSO_4.5H_2O$. This latter compound then goes into solution.

Let $CuSO_4 + 5H_2O = CuSO_4.5H_2O + x$ cals.

and $CuSO_4.5H_2O + Aq. = CuSO_4.5H_2O\ Aq.$

$$-\frac{249}{100} \times 1100 \text{ cals.}$$

When both these reactions take place together, we have :

$$CuSO_4 + Aq = CuSO_4.5H_2O\ Aq. + \frac{159 \times 9990}{100} \text{cals.}$$

$$\therefore \quad \frac{159 \times 9990}{100} = x - \frac{249}{100} \times 1100$$

Whence, $x = 18623$

∴ $CuSO_4 + 5H_2O = CuSO_4.5H_2O + 18623$ cals.

Example 5. *From the following data of Thomsen calculate the heat of formation of anhydrous aluminium chloride :—*

(*i*) $2Al + 6HCl\ Aq = Al_2Cl_6\ Aq + 3H_2 + 239760$ *cals.*

(*ii*) $H_2 + Cl_2 = 2HCl + 44000$ *cals.*

(*iii*) $HCl + Aq = HCl\ Aq. + 17315$ *cals.*

(*iv*) $Al_2Cl_6 + Aq = Al_2Cl_6\ Aq + 153690$ *cals.*

Heat of formation of HCl = 22000 cal.

Heat of solution of HCl = 17315 cal.

∴ Heat of formation of HCl Aq = 39315 cal.

and the intrinsic energy of HCl Aq = − 39315 cal.

Substituting this value in the equation

$$2Al + 6HCl\ Aq = Al_2Cl_6\ Aq + 3H_2 + 239760 \text{ cal.}$$

we get

$$0 - 6 \times 39315 = -x + 0 + 239760$$

where x is the heat of formation of Al_2Cl_6 Aq.

Solving the equation for x we get :

$$x = 475650 \text{ cal.}$$

Substituting this value in the last equation we can find out y; the heat of formation of Al_2Cl_6 :—

$$Al_2Cl_6 + Aq = Al_2Cl_6\ Aq + 153690 \text{ cal.}$$

Whence y = **321960 cal.**

Alternative Method. Multiplying equations *(ii)* by 3 and *(iii)* by 6, and adding up all the four equations we directly get the heat of formation of anhydrous aluminium chloride:—

$$2Al + 6HCl\ Aq = Al_2\ Cl_6\ Aq + 3H_2 + 239760 \text{ cal.}$$

$$3H_2 + 3Cl_2 = 6HCl + 3 \times 44000 \text{ cal.}$$

$$6HCl + Aq = 6HCl\ Aq + 6 \times 17315 \text{ cal.}$$

$$Al_2\ Cl_6 + Aq = Al_2Cl_6\ Aq + 153690 \text{ cal.}$$

$$2Al + 3Cl_2 = Al_2Cl_6 + \mathbf{321960\ cal.}$$

Example 6. *Calculate the heat of formation of* SO_3 *from the following experimental data of Hess :—*

(i) $PbO + S + 3O = PbSO_4 + 165500$ *cals.*

(ii) $PbO + H_2SO_4.\ Aq = PbSO_4 + Aq + 23300$ *cals.*

(iii) $SO_3 + Aq = H_2SO_4\ Aq + 41100$ *cals.*

Subtracting equation *(ii)* from *(i)* we get

(*iv*) $S + 3O - H_2SO_4\ Aq = 165500 - 23300$ cals.
$= 142200$ cals.

Equation (*iii*) can be written in the following form

(*v*) $SO_3 - H_2SO_4\ Aq = 41100$ cals.

Subtracting (*v*) from (*iv*) we get

$S + 3O - SO_3 = 101100$ cals.

Transposing SO_3 we get

$S + 3O = SO_3 + 101100$ cals.

which means that the heat of formation of SO_3

$= 101100$ cals.

Example 7: *Find the heat of formation of* PCl_3 *from its elements from the following data :—*

(*i*) $PCl_3 + 3H_2O + Aq = P(OH)_3\ Aq + 3HCl\ Aq + 651{\cdot}1\ Cal.$

(*ii*) $H_2 + Cl_2 + Aq = 2HCl\ Aq + 786{\cdot}0\ Cal.$

(*iii*) $2P + 3O + 3H_2O + Aq = 2P(OH)_3Aq + 2504{\cdot}0\ Cal.$

(*iv*) $H_2 + O = H_2O + 683{\cdot}57\ Cal.$ (*Punjab B.Sc.* 1931.)

Heat of formation of HCl Aq $= 393{\cdot}0$ Cal.

$\therefore$ Its intrinsic energy $= -393{\cdot}0$ Cal.

The intrinsic energy of $H_2O = -683{\cdot}57$ Cal.

Let the intrinsic energy of $P(OH)_3$ Aq $= x$ Cal.

Substituting these values in equation (*iii*) we get

$0 + 0 - 3 \times 683{\cdot}57 + 0 = 2x + 2504{\cdot}0$

$\therefore \quad x = -2277{\cdot}35$ Cal.

Substituting this and other values of intrinsic energies in equation (*i*) we get

$PCl_3 + 3H_2O + Aq = P(OH)_3\ Aq + 3HCl\ Aq + 651{\cdot}0$ Cal.

$y - 3 \times 683{\cdot}57 + 0 = -2277{\cdot}35 - 3 \times 393 + 651$, where y is the intrinsic energy of PCl_3.

Whence $y = -754{\cdot}65$ Cal.

$\therefore$ Heat of formation of $PCl_3 = 754{\cdot}65$ Cal.

Alternative Method. Rewriting equations (*i*) and (*iii*) so that P may appear on the left and PCl_3 on the right hand side, multiplying (*i*) by 2 and (*ii*) and (*iv*) by 3, and finally adding up all the equations we directly get the heat of formation of PCl_3 :—

$$2P(OH)_3Aq + 6HClAq = 2PCl_3 + 6H_2O + Aq - 2 \times 651{\cdot}0 \text{ Cal.}$$

$$3H_2 + 3Cl_2 + Aq = 6HCl\ Aq + 3 \times 786{\cdot}0 \text{ Cal.}$$

$$2P + 3O + 3H_2O + Aq = 2P(OH)_3\ Aq + 2504{\cdot}0 \text{ Cal.}$$

$$3H_2O = 3H_2 + 3O - 3 \times 683{\cdot}57 \text{ Cal.}$$

$$2P + 3Cl_2 = 2PCl_3 + 1509{\cdot}3 \text{ Cal.}$$

$$\therefore \quad P + 3Cl = PCl_3 + \mathbf{754{\cdot}65\ Cal.}$$

42. Heat of Reaction at constant Volume and at Constant Pressure. There is one peculiarity of gaseous reactions which needs special mention. When a gaseous reaction occurs at constant volume, no work is done by the gas or upon it, since there is neither expansion nor contraction. If however the reaction proceeds at constant pressure, then during expansion of the gaseous mixture work will be done by the gas and a part of the energy of the reaction equivalent to this work will be used up in this expansion and it will consequently appear too low. If the reaction proceeds with contraction of volume, work will be done on the gas and the heat thus produced comes out along with the heat of reaction, which will therefore appear too high.

When G. M. V. of a gas (or gaseous mixture) expands to 2 G. M. V., the work done

$$= \text{Pressure} \times \text{Increase of volume of the gas}$$

$$= P\ (2V - V) = PV = RT$$

As we are dealing with gram-molecules, R represents the gas constant and its value is approximately equal to 2 calories. There will therefore be an absorption of $2T$ calories of heat (where T is the absolute temperature of the gaseous mixture) for every gram-molecular volume increase in the reacting gases. During contraction $2T$ calories will be evolved for every gram molecular volume decrease in the volume of gases. In a chemical equation, the increase or

decrease in the number of molecules will be a measure of the increase or decrease in gram-molecular volumes. In thermochemical calculations generally heats at constant pressure are given, and these corrections are needed when heats of reaction at constant volume are required.

Example 8. *The heats of combustion of one gram-atom of carbon and one gram molecule of carbon monoxide are* 97000 *and* 68000 *calories respectively at constant pressure and at* 18°*C. Calculate the heat of formation of CO at constant pressure and at constant volume.*

$$(i) \quad C + O_2 = CO_2 + 97000 \text{ cal.}$$

$$(ii) \quad CO + \tfrac{1}{2}O_2 = CO_2 + 68000 \text{ cal.}$$

Substracting (*ii*) from (*i*) we get

$$C + \tfrac{1}{2}O_2 - CO = 29000 \text{ cal.}$$

or,
$$C + \tfrac{1}{2}O_2 = CO + 29000 \text{ cal.}$$

at constant pressure.

In this reaction, one-half volume has expanded to one volume, and work has been done in expansion. The heat absorbed will be equal to $= NRT = \frac{1}{2} \times 2 \times 291 = 291$ cals.

∴ Heat of formation of CO at constant volume $=$ $29000 + 291 = 29291$ cals.

Example 9. *The heat of formation of water is* 68360 *cal. and of carbon dioxide is* 96960 *cal., both at* 17° *and at constant pressure. The heat of combustion of methane at* 17° *and at constant pressure is* 211930 *cal. Calculate the heat of formation of methane at* 17°*C* (*a*) *at constant pressure* (*b*) *at constant volume.* (*Bombay B.A.*)

$$C + O_2 = CO_2 + 96960 \text{ cal.}$$

$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68360 \text{ cal.}$$

∴ Intrinsic energies of CO_2 and H_2O are -96960 and -68360 calories respectively.

Substituting these values in the following equation we can find out x, the heat of formation of CH_4 at constant pressure :—

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 211930 \text{ cal.}$$

$$-x + 0 = -96960 - 2 \times 68360 + 211930$$

$$\therefore \quad x = 21750 \text{ cal.}$$

To determine the heat of formation at constant volume

$$C + 2H_2 = CH_4 + y \text{ cal.}$$

we must subtract the heat which is evolved on account of contraction from two to one gram molecular volume.

Heat liberated $= nRT$

$= 1 \times 2 \times 290$

$= 580.$

Heat of formation of CH_4 at constant volume

$= 21750 - 580$ cal.

$= 21170$ cal.

EXERCISES

1. Calculate the heat of formation of ethylene, given that its heat of combustion is 341,100 calories, and that

$C + O_2 = CO_2 + 94{,}400$ calories.

$2H_2 + O_2 = 2H_2O$ (liquid) $+ 136{,}800$ calories. (*All. B.Sc.* 1917.)

2. State Hess's Law of thermochemistry. Calculate the heat of formation of formic acid from the following data :—

Heat of combustion of carbon (C, O_2) = 96960 cal.
„ „ „ „ Hydrogen (H_2, O) = 68360 „
„ „ „ „ formic acid ($HCOOH, O_2$) 65900 „

(*Punjab B.Sc.* 1921.)

3. How is the heat of formation of a compound usually determined ? Given that

$K + Aq = KOH\ Aq + \frac{1}{2}H_2 + 481$ Cal.

$H_2 + \frac{1}{2}O_2 = H_2O + 684$ Cal.

$KOH + Aq = KOH\ Aq + 133$ Cal.

Find the heat of formation of KOH from its elements.

(*Bombay B.A.*)

4. What is meant by exothermic and endothermic reactions ? From the thermal data below, show that dry hydrogen sulphide and iodine will not react.

(*i*) $H_2 + S$ (gas) $= H_2S + 4600$ cal.

(*ii*) $\frac{1}{2}H_2 + \frac{1}{2}I_2$(gas) $= HI - 6200$ cal.

Under what conditions can the reaction be brought about ?
(*Bombay B.A.*)

5. From the following data, calculate the thermal effect produced by the decomposition of ozone by hydrogen peroxide :—

$(H_2, O) = 68000$ cal.
$(H_2, O_2) = 45000$,,
$(O_2, O) = -30000$,,

(*Hons. Vict.* 1894.)

6. Find the heat of formation of acetaldehyde, (*i*) gaseous (*ii*) liquid, from the following data :—

$(2CH_3CHO, 5O_2)$ liquid $= 551$ Cal.
$(2CH_3.CHO, 5O_2)$ gaseous $= 564$,,
$(C, O_2) = 97$,,
$(2H_2, O_2)$ to water $= 136{\cdot}7$,,

(*B.Sc. Hons. Manc.* 1908.)

7. Calculate the heat of combination of calcium and oxygen from the following equations:—

$CaO + 2HCl = CaCl_2 + H_2O + 52{\cdot}7$ Cal.
$Ca + Cl_2 = CaCl_2 + 169{\cdot}8$ Cal.
$H_2 + \frac{1}{2}O_2 = H_2O + 57{\cdot}9$ Cal.
$H_2 + Cl_2 = 2HCl + 44{\cdot}0$ Cal.

(*Inst. Chem.*, 1907.)

8. Calculate the molecular heat of reduction of ethylene to ethane, given the following data :—

Molecular heat of combustion of hydrogen $= 64{\cdot}49$ Cal.
,, ,, ,, ,, ,, ethane $= 369{\cdot}0$ Cal.
,, ,, ,, ,, ,, ethylene $= 332{\cdot}2$ Calf

(*Hons., Manc.*, 1910"

9. From the following figures of Thomsen, find the heats of formation of ferric and ferrous chlorides from their elements :—

$$[Fe, 2HCl] = 21320 \text{ cal.}$$
$$[FeCl_2\ Aq, Cl] = 27770 \text{ ,,}$$
$$[FeCl_2, Aq] = 17900 \text{ ,,}$$
$$[H, Cl] = 22000 \text{ ,,}$$
$$[HCl, aq] = 17314 \text{ ,,}$$

10. From the following data, calculate the heat of formation of solid potassium chloride from its elements :—

(*i*) $KOH\ Aq + HCl\ Aq = KCl\ Aq + H_2O + 137{\cdot}5$ Cal.

(*ii*) $H_2 + Cl_2 + Aq = 2HCl\ aq + 786$ Cal.

(*iii*) $2H_2 + O_2 = 2H_2O + 1368$ Cal.

(*iv*) $2K + 2H_2O + Aq = 2KOH\ Aq + H_2 + 962$ Cal.

(*v*) $KCl + Aq = KCl\ aq - 44$ Cal.

(*B. Sc. Hons., Vict.*, 1902.)

11. The heat of formation of hypochlorous acid has been determined by two independent methods by Thomsen; his results are given below. From both sets, calculate the heat of formation of an aqueous solution of the acid (H, Cl, O, Aq).

A
$(2NaOH\ Aq, Cl_2) = 24647$ cal.
$(NaOH\ Aq, HClO\ Aq) = 9976$ cal.
$(NaOH\ Aq, HCl\ Aq) = 13740$,,

B
$(HClO\ Aq, 2HI\ Aq) = 51435$ cal.
$(H, I, Aq) = 13171$,,
$(H, Cl, Aq) = 39315$ cal.
$(H_2, O) = 68357$,,

(*London Hons.*, 1907.)

12. From the following data, based on the use of seminormal solutions throughout, calculate the heat which should be liberated in the production, in aqueous solution, of one gram molecule of ammonium acetate. 250 c.c. of caustic soda mixed with an equal volume of hydrochloric acid liberate 1710 calories ; the same volumes of caustic soda and acetic acid liberate 1620 calories, and of

ammonia and hydrochloric acid 1530 calories, for the purpose of calculation it is assumed that, in the solutions employed, the caustic soda and hydrochloric acid are fully dissociated. (*B.Sc., London* 1910.)

13. From the appended equations, calculate the heat of formation of ammonia from gaseous hydrogen and nitrogen (*a*) in the dry state, (*b*) in solution in water.

(*i*) $4NH_3 + 3O_2 = 2N_2 + 6H_2O + 362{,}400$ cals.

(*ii*) $2H_2 + O_2 = 2H_2O + 136{,}800$ cals.

(*iii*) $NH_3 + aq = NH_3\ aq + 8{,}400$ cals.

(*Camb. Tripos.*)

14. Calculate the heat of formation of $ZnCl_2$ solution from the following data :—

(*a*) $Zn + 2HCl\ aq = ZnCl_2\ aq + H_2 + 34{\cdot}4$ Cal.

(*b*) The heat of formation of an aqueous solution of hydrochloric acid is given by the equation.

$H_2 + Cl_2 = 2HCl + 78{\cdot}6$ Cals. (*Cal. B.Sc.* 1925.)

15. The heat of formation of carbon dioxide is 96,000 cals. When 24·32 gms. of magnesium are burned in carbon dioxide, carbon and magnesium oxide are formed, and 47000 cals. are evolved. Calculate the heat of formation of magnesium oxide. (*Bombay B.Sc.* 1912.)

16. From the following thermochemical equations, all of which refer to a temperature of 17°C, calculate the heat evolved in the polymerisation of acetylene to benzene, (*a*) at constant pressure, (*b*) at constant volume :—

$$C + O_2 = CO_2 + 96960 \text{ cals.}$$
$$2H_2 + O_2 = 2H_2O \text{ (liquid)} + 136720 \text{ cal.}$$
$$2C_6H_6 + 15O_2 = 12CO_2 + 6H_2O \text{ (liquid)} + 1598700 \text{ cal.}$$
$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O \text{ (liquid)} + 620100 \text{ cal.}$$

(*B. Sc. Sheffield.*)

17. Calculate the heats of formation of ethane, ethylene and acetylene at 17°C (*a*) at constant pressure (*b*) at constant volume from the following :—

$$C + O_2 = CO_2 + 96960 \text{ cals.}$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O \text{ (liquid)} + 68340 \text{ cals.}$$

$C_2H_6 + \frac{7}{2}O_2 = 2CO_2 + 3H_2O$ (liquid) + 370400 cals.
$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$ (liquid) + 333350 ,,
$C_2H_2 + \frac{5}{2}O_2 = 2CO_2 + H_2O$ (liquid) + 310000 ,,

ANSWERS.

1. − 15·5 Cal.
2. 99420 cal.
3. 1032 Cal.
5. + 53000 cal.
6. (*i*) 48·7 Cal.
(*ii*) 55·2 Cal.
7. 131 Cal.
8. 27·7 Cal.
9. $FeCl_3$, 82048 cal. ; $FeCl_2$, 96038 cal.
10. 1055·5 Cal.
11. A = 29973 cal. ; B = 29895 cal.
12. 11520 cals.
13. (*a*) = 12000 cals. ; (*b*) = 20400 cals.
14. 113 Cals.
15. 95000 cals.
16. (*a*) = 130800 cal. ; (*b*) 129640 cal.
17.

	At Constant Pressure.	*At Constant Volume.*
C_2H_6	28540 cal.	27090 cal.
C_2H_4	− 2750 ,,	− 3910 ,,
C_2H_2	− 47740 ,,	− 48610 ,,

CHAPTER VIII

ELECTROCHEMISTRY

43. Units of Electrical Energy. Electrical energy is measured in (1) the *quantity* factor, the unit of which is called the **coulomb**, and (2) the *intensity* factor, or the difference in potential, the unit of which is called the **volt.** The quantity of electrical energy flowing through a wire is the product of quantity factor by the intensity factor the unit being termed the **joule** :

NO. OF COULOMBS × NO. OF VOLTS = NO. OF JOULES.

The practical unit of current strength is the **ampere** which represents a current flowing at the rate of one coulomb per second.

The rate at which work is done by a current, or the **power**, is equal to the quantity of electricity carried per second multiplied by the voltage. The unit of power, 1 joule per second, is called a volt ampere, or a **watt.**

NO. OF AMPERES × NO. OF VOLTS = NO. OF WATTS.

Since watt is a small unit, in actual practice electrical energy is usually measured in **killowatt hours** (K.W.H.), *i.e.*, number of killowatts (1000 watts) expended per hour.

44. Faraday's Laws of Electrolysis. These may be stated as follows :—

First Law. *The quantity of an electrolyte decomposed by an electric current is proportional to the quantity of electricity which passes through the electrolyte.*

Second Law. *The quantities of different electrolyter decomposed by the same quantity of electricity are proportional to their chemical equivalents.*

The quantity of electricity required for the decomposition of 1 gram-equivalent of any electrolyte, or for the liberation of 1 gram-equivalent of any cation or anion, has been found to be equal to **96540 coulombs.** This is termed the **faraday.**

Example 1. *A current of* 5·6 *amperes is passed for* 1 *hour through a solution of cupric sulphate, using platinum electrodes. What weights of substances will be liberated at the two electrodes ?*

On electrolysis, copper will be liberated at the cathode. The sulphate radical set free at the anode will react with water and liberate oxygen :—

$$2SO_4 + 2H_2O \longrightarrow 2H_2SO_4 + O_2.$$

The total quantity of current that has passed through the solution

$$= 5{\cdot}6 \times 60 \times 60 \text{ coulombs}$$

$$= 20160 \text{ coulombs}$$

The equivalent weight of Cu = 31·8

" " O_2 = 8

Now, 96540 coulombs liberate 1 gram-equivalent of each of copper and oxygen. Hence the weights of these substances liberated are :

$$\text{Copper} = \frac{20160}{96540} \times 31{\cdot}8 = \mathbf{6{\cdot}41 \text{ gm.}}$$

$$\text{Oxygen} = \frac{20160}{96540} \times 8 = \mathbf{1{\cdot}614 \text{ gm.}}$$

Example 2. *A current when passed for 2 hours through a silver voltameter liberated* 0·240 *gm. of silver. What was the average value of the current ?*

Let C be the average value of the current in amperes. The total quantity of electricity that has passed through the voltameter

$$= C \times 2 \times 60 \times 60 \text{ coulombs.}$$

Now, 96540 coulombs liberate 1 gram-equivalent, *i.e.*,

108 gm. of silver. The quantity of silver that would be liberated by $C \times 2 \times 60 \times 60$ coulombs

$$= \frac{C \times 2 \times 60 \times 60}{96540} \times 108 \text{ gm.}$$

But the quantity of silver actually liberated = 0·240 gm

Equating these two values, we get :

$$\frac{C \times 2 \times 60 \times 60}{96540} \times 108 = 0{\cdot}240$$

whence $C = {\cdot}0298$ amperes.

45. Specific, Equivalent, and Molecular Conductivity. The *specific resistance* of a conductor is the resistance in *ohms* of 1 centimeter cube of that substance. The definition applies to liquids as well as to solids. In the case of liquids, it is the resistance of a column of the material contained between two parallel metallic electrodes of area 1 sq. cm. and placed 1 cm. apart.

The reciprocal of the specific resistance of a conductor is called its *specific conductivity* (generally denoted by κ and is measured in *mhos* or *reciprocal ohms* (**r.o.**)

The conductivity of an aqueous solution of an electrolyte is generally expressed as **equivalent conductivity**, by which is meant *the specific conductivity of the solution multiplied by the volume of the solution in c. cs. which contains 1 gram-equivalent of the electrolyte.* The equivalent conductivity of a solution is usually denoted by λ.

Kohlrausch found that on dilution, the equivalent conductivity gradually increases to a maximum value, called the **equivalent conductivity at infinite dilution**, usually denoted by λ_∞.

Besides the equivalent conductivity, the term **molecular conductivity**, μ is sometimes used. This is the

specific conductivity of a solution multiplied by the volume in c. cs. which contains 1 *mol* of the electrolyte. The molecular conductivity at infinite dilution is expressed by $\mu\infty$.

The equivalent conductivity of the aqueous solution of an electrolyte at a given dilution. which may be represented by λv is proportional to the number of the free ions, and hence to the **degree of dissociation** α. At infinite dilution, the dissociation is complete, *i. e.*, $\alpha = 1$. Hence we have :

$$\frac{\alpha}{1} = \frac{\lambda v}{\lambda \infty}$$

$$\text{or } \alpha = \frac{\lambda v}{\lambda \infty}$$

The above relation is employed to calculate the degree of ionization from conductivity measurements.

Example 3. *The resistance of a column of solution* 3·5 *cm. long and of cross-section* 2·0 *sq. cm. is* 26·0 *ohms. What is the specific conductivity of the solution.*

Since the resistance of a conductor is proportional to its length and inversely proportional to its cross-section, we have ;

$$\text{Specific Resistance of the solution} = \frac{26{\cdot}0 \times 2{\cdot}0}{3{\cdot}5} \text{ ohms.}$$

$$\therefore \text{ Its Specific Conductivity} = \frac{3{\cdot}5}{26{\cdot}0 \times 20} \text{ rec. ohms.}$$

$$= {\cdot}6073 \text{ rec. ohms.}$$

Example 4. *The specific resistance of a solution of hydrochloric acid containing* 50 *grams of HCl. per litre is* 2·5 *ohms at* 20°*C. Given that the equivalent conductivity of the acid at infinite dilution is* 380 *rec. ohms, calculate the degree of ionization of the given solution.*

$$\text{Specific conductivity of the solution} = \frac{1}{2{\cdot}5} \text{ rec. ohms.}$$

Volume in c. c. that contains 1 gram-equivalent o

$$\text{HCl} = \frac{1000 \times 36{\cdot}5}{50}$$

$$\therefore \text{ Equivalent conductivity} = \frac{1}{2{\cdot}5} \times \frac{1000 \times 36{\cdot}5}{50} \text{ r.o}$$

$$= 292 \text{ r.o.}$$

$$\text{Hence, the degree of ionization} = \frac{292}{380} = \mathbf{0{\cdot}769.}$$

Example 5. *The specific conductivity of a* 5 *per cent barium chloride solution at* 20° *is* ·039 *rec. ohm, and its density* 1·044. *Calculate* (1) *the degree of ionization of the solution and* (2) *its freezing point. K for water is* 18·6 *and* $\lambda \infty$ *of* $BaCl_2$ *at* 20° *is* 120 *rec. ohms.*

(1) CALCULATION OF THE DEGREE OF IONIZATION

$$\text{Volume of 100 gm. of the solution} = \frac{100}{1{\cdot}044} \text{ c. c.} = 95{\cdot}8 \text{ c.c.}$$

Volume of the solution in c. cs. that contains

$$\text{1 gram-equivalent of } BaCl_2 = \frac{95{\cdot}8 \times 104}{5}$$

$$\therefore \text{ Equivalent conductivity} = {\cdot}039 \times \frac{958 \times 104}{5} \text{ r. o.}$$

$$= 77{\cdot}7 \text{ r. o.}$$

$$\text{Degree of Ionization} = \frac{77{\cdot}7}{120} = \mathbf{0{\cdot}648.}$$

(2) CALCULATION OF THE FREEZING POINT :

Molecular weight of barium chloride = 208.

The quantity of barium chloride in 100 gm. of the solution = 5 gm.

K for water = 18·6

Substituting the above values in the formula

$$\frac{M}{s} = \frac{K}{\delta} \qquad \text{[Art. 20}$$

We get δ, the theoretical depression of the freezing point, assuming absence of ionization :

$$\delta = \frac{18{\cdot}6 \times 5}{208} = 0{\cdot}442.$$

Let $\triangle$ be the actual depression of the freezing point. We have :

$$x = -\frac{\triangle - \delta}{\delta(n-1)}$$ [Art. 15

where x represents the degree of ionization and n the number of ions into which a molecule of the electrolyte splits up, which in this case is 3. Hence we have :

$$0{\cdot}648 = \frac{\triangle - 0{\cdot}442}{0{\cdot}442 \times 2}$$

whence $\triangle = 1{\cdot}02$

$\therefore$ Freezing point of the solution $= -\mathbf{1{\cdot}02^{\circ}C.}$

46. Relative Speeds of Ions. When a salt solution is electrolyzed, the anion and the cation move in opposit directions with different speeds. This causes changes oe concentration of the salt round the electrodes. Thusf when cupric sulphate solution is electrolyzed between, platinum electrodes, the colour fades much more rapidly at the cathode than at the anode. Again, if a solution of silver nitrate be electrolyzed between silver electrodes, there occurs a transference of silver from the anode to the cathode, and, while the *total* concentration of the salt in solution remains unaltered, there occurs a fall of concentration round the cathode and a rise in concentration round trhe anode.

By using an apparatus so designed as to prevent the mechanical mixing of the dissolved salt between the two electrodes, the change in concentration round the electrodes can be experimentally determined, and from this the relative speeds of the two ions can be calculated with the help of the following relation :

$$\frac{\textbf{Speed of Cation}}{\textbf{Speed of Anion}} = \frac{\textbf{Fall round anode}}{\textbf{Fall round cathode}}$$

Example 6. *A current which deposited* 32·2 *mg. of silver in a silver voltameter was passed through a solution of silver nitrate using silver electrodes. The increase of concentration of* $AgNO_3$ *round the anode corresponded*

to 16·8 *mg. of silver. Calculate the speed ratio of cation and the anion.*

The fall in concentration round the cathode (which is equal to the rise in concentration round the anode, since the total quantity of $AgNO_3$ necessarily remains unaltered) = 16·8 mg.

Had no silver ions migrated from the anode, there would have occurred an increase of concentration equal to 32·2 mg. of silver.

The observed increase of concentration = 16·8 mg.

∴ Decrease of concentration due to the migration o silver ions = 32·2 − 16·8 mg. = 15·4 mg.

Hence,

$$\frac{\text{Speed of Ag.}}{\text{Speed of } NO_3'} = \frac{\text{Fall round anode}}{\text{Fall round cathode}} = \frac{15{\cdot}4}{16{\cdot}8} = \mathbf{0{\cdot}917.}$$

47. Transport Numbers of the Ions. Since the electric current is carried through a solution by the ions, which, as we have seen above, move with different velocities, the amount of the current carried by the cation must be different from that carried by the anion, the two quantities being proportional to the speeds of the cation and the anion respectively. If u is the speed of migration of the cation and v that of anion, $\frac{u}{u+v}$ represents the share taken by the cation in the transport of the current This is known as the **transport number** of the cation Similarly, $\frac{v}{u+v}$ is the transport number of the anion. The transport number of the *anion* is usually denoted by n. The transport number of the cation is therefore $1-n$ ince the sum of the two is equal to 1.

The transport number of an ion may be calculated directly from the fall of concentration round the two electrodes, as the fall around each electrode is proportional to the speed of the ion moving away from it. Thus, using the experimental results of Example 5 we have :

Transport number of silver ion

$$= \frac{\text{Fall due to the migration of silver ion}}{\text{Total fall in concentration}}$$

$$= \frac{15{\cdot}4}{32{\cdot}2} = 0{\cdot}478.$$

Similarly, the transport number of NO_3'

$$= \frac{\text{Fall due to the migration of nitrate ion}}{\text{Total fall in concentration}}$$

$$= \frac{16{\cdot}8}{32{\cdot}2} = 0{\cdot}522.$$

Example 7. *A current that deposited* ·0864 *gm. of silver in a silver voltameter was passed through a solution containing* 0·16 *per cent. of NaOH, using platinum electrodes. After electrolysis all the cathode solution was removed and was found to weigh* 60·8 *gm. and to contain* 0·1042 *gm. of NaOH. Calculate the transport numbers of Na· and OH′ ions.*

The amount of silver deposited in the voltameter = ·0864 gm.

∴ The total amount of NaOH that was decomposed during electrolysis $= {\cdot}0864 \times \frac{40}{108}$ gm. = 0·0320 gm.

Before electrolysis 100 grams of the cathode solution contained 0·16 gm. of NaOH. Hence, 60·8 gm. of the cathode solution contained $\frac{0{\cdot}16 \times 60{\cdot}8}{100}$ or ·09728 gm. NaOH.

After electrolysis 60·8 gm. of the cathode solution contained 0·1042 gm. of NaOH.

∴ Increase in the amount of NaOH round the cathode = 0·1042 − 0·09728 = ·00692 gm.

During the electrolysis the sodium ions discharged at the cathode react with water to reproduce their equivalent of NaOH.

The increase in the amount of NaOH round the cathode due to this secondary action would be equal to ·0320 gm. But the actual increase is less, *i.e.* ·00692 gm. The difference, *i.e.*, ·0320 − ·00692 or ·02508 gm. represents the fall in concentration due to the migration of OH′ ion.

$$\text{Transport number of OH}' \text{ ion} = \frac{\text{Fall due to the migration of OH}'}{\text{Total fall in concentration}}$$

$$= \frac{\cdot 02508}{\cdot 0320} = \mathbf{0 \cdot 784}.$$

$\therefore$ Transport number of $Na^{\cdot} = 1 - 0 \cdot 784 = 0 \cdot 216$.

Example 8. *A solution containing* 2·84 *per cent. of* $CuSO_4$ *was submitted to electrolysis using a platinum cathode and a copper anode. After electrolysis the cathode solution was found to weigh* 54·7 *grams and to contain* 0·409 *gm. of copper. The increase in weight of the cathode was* 0·408 *gm. Calculate the transport numbers of* $Cu^{\cdot\cdot}$ *and* SO_4'' *ions.* ($Cu = 63 \cdot 6$).

The total fall in concentration corresponds to 0·408 gm. of Cu.

Before electrolysis 100 gm. of the cathode solution contained 2·84 gm. of $CuSO_4$. Hence, 54·7 gm. of it contained $2 \cdot 84 \times \frac{54 \cdot 7}{100}$ or 1·553 gm. of $CuSO_4$, which corresponds to $1 \cdot 553 \times \frac{63 \cdot 6}{159 \cdot 6}$ or 0·619 gm. of Cu.

After electrolysis 54·7 gm. of the cathode solution contained 0·409 gm. of Cu.

$\therefore$ Fall in concentration round the cathode which is due to the migration of SO_4'' ions, corresponds to 0·619 − 0·409 gm. or 0·210 gm. of Cu.

$$\text{Transport number of } SO_4'' = \frac{\text{Fall due to the migration of } SO_4''}{\text{Total fall in concentration}}$$

$$= \frac{0 \cdot 210}{0 \cdot 408} = \mathbf{0 \cdot 515}.$$

Transport number of $Cu^{\cdot\cdot} = 1 - 0 \cdot 515 = \mathbf{0 \cdot 485}$.

48. Ionic Mobilities. From a study of the conductivity of dilute solutions of electrolytes Kohlrausch found that for solutions of strong electrolytes the equivalent conductivity at infinite dilution may be regarded as the sum of two independent factors, one pertaining to the cation and the other to the anion. This is known as **Kohlrausch's Law**, and is generally formulated as follows :

$$\lambda \infty = u + v$$

u and v, when expressed in proper units, are called the *ionic mobilities*. The relative values of u and v for an electrolyte can be calculated from the equivalent conductivity at infinite dilution and the transport numbers of the constituent ions.

The great practical utility of Kohlrausch's Law lies in the fact that by its help we can calculate $\lambda \infty$ for weak electrolytes, such as NH_4OH and CH_3COOH. In such cases it is not possible to determine $\lambda \infty$ directly from conductivity measurements, since the limiting value is not reached even at very great dilutions.

Example 9. *The equivalent conductivity at infinite dilution of* $AgNO_3$ *at* 18° *is* 115·5, *and the transport number of the silver ion in the salt is* 0·482. *Calculate the mobilities of the silver and the nitrate ions.*

Let u and v be the mobilities of the cation and anion espectively.

Since the transport numbers are proportional to the ionic mobilities, we have :

$$0{\cdot}482 = \frac{u}{u+v}$$

Now,

$$u + v = \lambda \infty = 115{\cdot}5$$

$$\therefore \quad \frac{u}{115{\cdot}5} = 0{\cdot}482$$

whence

$$u = \mathbf{55{\cdot}7}$$

$$v = \lambda \infty - u$$

$$= 115{\cdot}5 - 55{\cdot}7$$

$$= \mathbf{60{\cdot}8}.$$

Example 10. *At 15°C the equivalent conductivity at infinite dilution for HCl and CH_3COONa is 380 and 80 mhos respectively. The transport numbers for $H^{\cdot}$ and $Na^{\cdot}$ in these electrolytes are 0·84 and 0·56 respectively. Calculate the equivalent conductivity at infinite dilution for acetic acid.*

Mobility of $H^{\cdot} = \lambda\infty$ for HCl × transport number of $H^{\cdot}$

$= 380 \times 0{\cdot}84 = 319{\cdot}2$ mhos

Mobility of CH_3COO'

$= \lambda\infty$ for CH_3COONa × transport number of CH_3COO

$= 80 \times (1 - 0{\cdot}56) = 35{\cdot}2$ mhos

$\therefore$ $\lambda\infty$ for $CH_3COOH = 319{\cdot}2 + 35{\cdot}2$ mhos

$= \mathbf{354{\cdot}4}$ **mhos.**

49. Application of the Law of Mass Action to Ionic Equilibrium. Suppose we have one mol of a binary electrolyte dissolved in water so as to give V litres of solution. If the degree of ionisation is x, the active masses of the two kinds of ions and of undissociated molecules at equilibrium are $\frac{x}{V}$, $\frac{x}{V}$ and $\frac{1-x}{V}$ respectively.

Hence, the Law of Mass Action (Art. 22) assumes the form

$$\frac{\frac{x}{V} \times \frac{x}{V}}{\frac{1-x}{V}} = K$$

or

$$\frac{x^2}{(1-x)V} = \mathbf{K}.$$

This relationship is known as **Ostwald's dilution formula.** K is here known as the **ionisation constant.** *The formula is found to hold good only for weak electrolytes*, that is, only with such electrolytes does K remain constant with varying concentrations. Since in all these

cases x is small as compared with 1, the factor $1 - x$ may be taken to be practically equal to 1. Hence, we get the simplified formula

$$\frac{x^2}{V} = K.$$

Thus we see that *in the case of weak electrolytes, the degree of ionisation is approximately proportional to the square root of the dilution.*

The behaviour of strong electrolytes, *i.e.*, those having a high degree of ionisation, does not agree with Ostwald's dilution formula.

Example 11. *Ostwald determined the molecular conductivities of solutions containing one gram-molecule of acetic acid in v litres. The results obtained are tabulated below :—*

	v in litres.	*Molecular conductivity.*
(*i*)	8	4·34
(*ii*)	16	6·10
(*iii*)	64	12·09
(*iv*)	128	16·99
(*v*)	256	23·82

The conductivity at infinite dilution for acetic acid is 364. *Show that the results are in agreement with the dilution formula.*

The degrees of dissociation calculated from the relation $x = \frac{\lambda v}{\lambda \infty}$ are:

(*i*) $x = \frac{4{\cdot}34}{364}$ or ·0119.

(*ii*) $x = \frac{6{\cdot}10}{364}$ or 0·167.

(*iii*) $x = \frac{12{\cdot}09}{364}$ or ·0333.

(*iv*) $x = \frac{16{\cdot}99}{364}$ or ·0468.

(*v*) $x = \frac{23{\cdot}82}{364}$ or ·0656

The values of K calculated from the Dilution formula $K = \frac{x^2}{(1-x)V}$ are:

(*i*) $K = \frac{(\cdot 0119)^2}{(1 - \cdot 0119) \times 8}$ or ·0000179.

(*ii*) $K = \frac{(\cdot 0167)^2}{(1 - \cdot 0167) \times 16}$ or ·0000177.

(*iii*) $K = \frac{(\cdot 0333)^2}{(1 - \cdot 0333) \times 64}$ or ·0000179.

(*iv*) $K = \frac{(\cdot 0468)^2}{(1 - \cdot 0468) \times 128}$ or ·0000179.

(*v*) $K = \frac{(\cdot 0656)^2}{(1 - \cdot 0656) \times 256}$ or ·0000180.

Hence we see that the value of K is practically constant, and is independent of the concentration of solutions. The results obtained therefore are in close agreement with the Dilution formula.

Exercise. To get an idea as to the degree of approximation attained by the use of the simplified form of the dilution formula, the student may calculate the values of K in Example 10 from the equation $K = \frac{x^2}{V}$. He will find that the values are fairly concordant, and are practically the same as obtained from the formula

$$K = \frac{x^2}{(1-x)V}.$$

Example 12. *The ionization constant of a monobasic organic acid (mol. wt.=88) at 20°C is $1 \cdot 5 \times 10^{-5}$. Calculate the degree of ionization of (i) the N/5 solution of the acid and (ii) of a solution containing 2 gm. of the acid per litre.*

(*i*) Since the ionization constant is very low, *i.e.*, the acid is weak, we may apply the simplified form of the dilution formula:

$$\frac{x^2}{V} = K.$$

whence,

$$\frac{x^2}{5} = 1{\cdot}5 \times 10^{-5}$$

$$\therefore \quad x = \mathbf{{\cdot}00866.}$$

(*ii*) In the case of the solution containing 2 gm. of the acid per litre, V, the volume in litres that contains 1 gram-molecule of the acid is 88/2, or 44.

$$\therefore \quad \frac{x^2}{44} = 1{\cdot}5 \times 10^{-5}$$

whence $x = \mathbf{{\cdot}0257.}$

Example 13. *To 1 litre of N/100 acetic acid* ($K = 1{\cdot}8 \times 10^{-5}$), 1·64 *gm. of sodium acetate was added. Calculate the hydrogen ion concentration before and after the addition of the salt, on the assumption that the salt was completely ionized in solution.*

Since acetic acid is a weak acid. we may, in this example, employ the simplified dilution formula.

Let the degree of dissociation of the acid before the addition of sodium acetate be x. Then we have:

$$\frac{x^2}{\mathrm{V}} = K$$

$$\frac{x^2}{100} = 1{\cdot}8 \times 10^{-5}$$

whence $x = {\cdot}0424.$

The total concentration of the acid $= {\cdot}01$ mol. per litre.

$\therefore$ Concentration of hydrion before the addition of sodium acetate $= {\cdot}01 \times {\cdot}0424$ or $\mathbf{4{\cdot}24 \times 10^{-4}}$ **gm. equivalent per litre.**

The volume of the solution that contains 1 mol. of acetic acid = 100 litres.

The quantity of sodium acetate (mol. wt. = 82) added per 100 litres of the solution

$$= \frac{1{\cdot}64}{82} \times 100 = 2 \text{ mol.}$$

Let y be the degree of ionization of acetic acid after the addition of sodium acetate. Then we have :

$$\text{Total } [CH_3COOH] = \frac{1-y}{100} \text{ mol. per litre}$$

$$\text{,, } [H^{\cdot}] = \frac{y}{100} \text{ gm. equivalent per litre.}$$

$$\text{,, } [CH_3COO'] = \frac{2+y}{100} \text{ ,, ,,}$$

From the law of mass action we have :

$$\frac{[H^{\cdot}] \times [CH_3COO']}{[CH_3COOH]} = K = 1{\cdot}8 \times 10^{-5}$$

$$\therefore \quad \frac{y \times (2+y)}{(1-y) \times 100} = 1{\cdot}8 + 10^{-5}$$

Now, since y is a very small fraction, $2+y$ is practically equal to 2 and $1-y$ is practically equal to 1.

$$\therefore \quad \frac{2y}{100} = 1{\cdot}8 + 10^{-5}$$

$$y = 9 \times 10^{-4}$$

Hence $[H^{\cdot}]$, the concentration of hydrion *after* the addition of sodium acetate

$$= \frac{9 \times 10^{-4}}{100} = \mathbf{9 \times 10^{-6}} \quad \textbf{gram-equivalent per litre.}$$

51. Hydrogen Ion Concentration, pH Values. Pure water is very slightly ionized :

$$H_2O \rightleftharpoons H^{\cdot} + OH'$$

By the mass action law we have :

$$\frac{[H^{\cdot}] \times [OH']}{[H_2O]} = K$$

Now, since the degree of ionization of pure water is very small, the concentration of undissociated water is practically constant. Hence,

$$[H'] \times [OH'] = Kw,$$

i.e., in pure water, or in any dilute solution, the product

of the concentrations of $H^{\cdot}$ and OH' (known as the "**ionic product**" for water, and usually devoted by Kw) is always constant. The value of this constant at 22° is 1×10^{-14}, when the concentrations are expressed in gram ions per litre. In pure water, therefore, the concentrations of $H^{\cdot}$ and OH' are both equal to 1×10^{-7} gram-ions per litre.

The ionic product for water remains constant, even when an electrolyte is dissolved in it. In a neutral solution, the two concentrations are identical; on the addition of an acid, the hydrogen ion concentration increases, while the hydroxyl ion concentration proportionately decreases. Thus in an N/1000 solution of HCl, which may be assumed to be almost completely ionized, $[H^{\cdot}] = 1 \times 10^{-3}$ gram ion per litre. But since, $[H^{\cdot}] \times [OH'] = 10^{-14}$, $[OH']$ must be equal to 1×10^{-11} gram ion per litre.

From the above it follows that the acidity or alkalinity of any solution can be expressed by the concentration of the hydrogen ions alone. If the latter is higher than 1×10^{-7} the solution is acidic, if lower, it is alkaline.

The concentration of hydrion is now universally expressed as pH values. The pH value of N/1000 HCl, referred to above, is 3. Similarly, the pH value of a solution whose hydrogen ion concentration is 1×10^{-5} is 5, and that of a solution whose hydroxyl ion concentration is 10^{-8} is 14–8 or 6. The pH value of a solution whose hydrogen ion concentration is C gram ion per litre is given by the relation :

$$p\mathrm{H} = \log_{10}\left(\frac{1}{C}\right)$$

i.e., the pH value of a solution is the *logarithm of the reciprocal of the hydrogen ion concentration*, the logarithm being always expressed as a quantity of *one sign only*, and not, as is usually done in arithmetical calculations, by a negative characteristic and positive mantissa.

Example 14. *In a* 0·1 *N solution of acetic acid the degree of ionization is* ·013. *Calculate* (1) *the hydrogen*

ion concentration of the solution, (2) *the hydroxyl ion concentration, and* (3) *its pH value.*

(1) The total concentration of the acid = 0·1 mol. per litre.

Degree of ionization = ·013

∴ The hydrogen ion concentration

$= 0{\cdot}1 \times {\cdot}013 = \mathbf{1{\cdot}3 \times 10^{-3}}$ **gm. ion per litre.**

(2) Since the ionic product for water is 1×10^{-14} we have :

$$[H^{\cdot}] \times [OH'] = 1 \times 10^{-14}$$

$$\therefore [OH'] = \frac{1 \times 10^{-14}}{1{\cdot}3 \times 10^{-3}} = 0{\cdot}77 \times 10^{-11}$$

$$= \mathbf{7{\cdot}7 \times 10^{-12}} \textbf{ gram ion per litre.}$$

(3) Substituting the value of the hydrogen ion concentration in the formula :

$$pH = \log \frac{1}{C}$$

We have :

$$pH = \log \frac{1}{1{\cdot}3 \times 10^{-3}}$$

$$= \log \frac{10^3}{1{\cdot}3} = \log 10^3 - \log 1{\cdot}3$$

$$= \mathbf{2{\cdot}886}$$

Example 15. *The pH number of an acid solution is* 3·42. *Calculate the hydrion concentration in gram equivalents per litre.*

We have :

$$\log \frac{1}{[H^{\cdot}]} = pH = 3{\cdot}42.$$

The antilog of 3·42 = 2630

$$\therefore \frac{1}{[H^{\cdot}]} = 2630$$

$$\text{or } [H^{\cdot}] = \frac{1}{2630} = \mathbf{3{\cdot}8 \times 10^{-4}} \textbf{ gm. equivalent per litre}$$

52. Indicators. A convenient method for the determination of hydrogen ion concentration is based on the use of indicators. An indicator undergoes a change of colour in aqueous solution only when the concentration of the hydrion exceeds a certain definite value which is characteristic for that indicator. Thus, litmus changes from blue to red when the hydrion concentration is greater than 10^{-7}, while methyl orange changes from yellow to pink when the hydrion concentration exceeds 10^{-5}. The following table shows the change in colour of some common indicators as the hydrion concentration increases and the minimum hydrion concentration and the pH values at which the change occurs:

Indicator.	Colour change.	[H·]	pH
Trinitrobenzene	orange to colourless	10^{-13}	13
Phenolphthalein	pink to colourless	10^{-9}	9
Litmus	blue to red	10^{-7}	7
Methyl red	yellow to red	10^{-6}	6
Methyl orange	yellow to pink	10^{-5}	5
Congo red	red to blue	10^{-4}	4

In order to determine the pH value of a solution we need several indicators which change colour at different hydrion concentrations. A little of each of the indicators is added to separate portions of the solution under examination, until one of the indicators shows the solution to be *acid* and the next in the list shows it to be *alkaline*. Thus, if the solution is acid towards methyl red and alkaline towards methyl orange, the pH value is between 5 and 6. By comparing the tint obtained with standard solutions, the pH value can be very accurately determined.

53. Hydrolysis of Salts. In an aqueous solution, the salts of weak acids and weak bases undergo "hydrolysis", which consists in the interaction of the salt with water to produce free acid and free base:

$$BA + H_2O \rightleftharpoons HA + BOH$$

The formulae for hydrolysis may be established as given below, where we assume

(1) that strong electrolytes are practically completely ionized,

(2) that the weak acids and the weak bases, produced as the result of hydrolysis, are practically undissociated, a condition which will be almost entirely fulfilled in the presence of a large excess of kation and anion from the salt,

(3) that the ionization of weak acids and weak bases is controlled by Ostwald's dilution formula, and

(4) that the active mass of water in the solution remains constant.

Case I. Hydrolysis of a Salt of a Weak Acid with a Strong Base. To take a concrete example, let us consider the hydrolysis of sodium acetate,

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH,$$

which, for the present purpose, may be represented as follows :

$$CH_3COO' + Na^{\cdot} + H_2O \rightleftharpoons CH_3COOH + Na^{\cdot} + OH'$$

or
$$CH_3COO' + H_2O \rightleftharpoons CH_3COOH + OH'$$

Since the concentration of water in the solution remains constant, we have :

$$\frac{[CH_3COOH] \times [OH']}{[CH_3COO']} = K_H \text{ (hydrolysis constant)}$$

Let 1 mol. of sodium acetate be dissolved in V litres, and let x mol. be the amount of the salt that has been hydrolyzed. Then we have

$$[CH_3COOH] = [OH'] = \frac{x}{V} \text{ mol per litre.}$$

$$[CH_3COO'] = \frac{1-x}{V} \quad \text{,,} \quad \text{,,}$$

Substituting these values in the above equation we get

$$\frac{\frac{x^2}{V^2}}{\frac{1-x}{V}} = \frac{x^2}{(1-x)V} = K_H \ldots\ldots\ldots\ldots (1)$$

Now, in the reaction

$$CH_3COOH \rightleftharpoons CH_3COO' + H^{\cdot}$$

$$\frac{[CH_3COO'] \times [H^{\cdot}]}{[CH_3COOH]} = K_A \text{ (ionization constant of acid).}$$

$$\therefore \qquad [H^{\cdot}] = K_A \times \frac{[CH_3COOH]}{[CH_3COO']}$$

$$= K_A \times \frac{x}{1-x}$$

Also, $[OH'] = \frac{x}{V}$

Hence, for the ionic product of water we have

$$K_w = [H^{\cdot}] \times [OH']$$

$$= K_A \times \frac{x}{1-x} \times \frac{x}{V} = K_A \times \frac{x^2}{(1-x)V} \ldots\ldots (2)$$

From equations (1) and (2) we get

$$K_H = \frac{x^2}{(1-x)V} = \frac{K_w}{K_A}$$

We may therefore calculate the degree of hydrolysis of a salt in aqueous solution from K_w and K_A, which can be experimentally determined by conductivity measurements.

Note. If the hydrolysis constant K_H and, therefore, the degree of hydrolysis x, is very small, *i.e.*, if K_A is very much greater than K_w, $1 - x$ may be put equal to 1 without introducing an appreciable error.

Hence, from equation (1) we get the simplified relation

$$\frac{x^2}{V} = K_H$$

Case II. Hydrolysis of a Salt of a Weak Base with a Strong Acid. This is exactly analogous to Case I, and we have the hydrolysis formula

$$K_H = \frac{K_W}{K_B} = \frac{x^2}{(1-x)V}.$$

where K_H is the hydrolysis constant of the salt, K_B the ionization constant of the weak base, x the degree of hydrolysis of the salt and V the volume of the solution, which contains 1 gram-molecule of the salt.

As in Case I, if K_B is very much greater than K_W $1-x$ may be put equal to 1, without introducing an appreciable error :

$$\frac{x^2}{V} = K_H.$$

Case III. Hydrolysis of a Salt of a weak Acid with a Weak Base. As an example of this, we may consider the hydrolysis of ammonium acetate, which may be represented as follows :—

$$NH_4^{\cdot} + CH_3COO' + H_2O = NH_4OH + CH_3COOH.$$

As before, let 1 mol. of the salt be dissolved in V litres and let x be the degree of hydrolysis.

By the mass-action law we have the hydrolysis equation

$$K_H = \frac{[NH_4OH] \times [CH_3COOH]}{[NH_4^{\cdot}] \times [CH_3COO']} = \frac{\frac{x^2}{V^2}}{\frac{(1-x)^2}{V^2}} = \frac{x^2}{(1-x)^2} \ldots\ldots(1)$$

In the case of the reaction

$$CH_3COOH \rightleftharpoons CH_3COO' + H^{\cdot}$$

we have

$$\frac{[CH_3COO'] \times [H^{\cdot}]}{[CH_3COOH]} = K_A \text{ (ionization constant of acid)}$$

whence

$$[H^{\cdot}] = K_A \times \frac{[CH_3COOH]}{[CH_3COO']}$$

$$= K_A \times \frac{x}{1-x}$$

Similarly, in the case of the reaction

$$NH_4OH \rightleftharpoons NH_4^{\cdot} + OH'$$

we have

$$\frac{[NH_4^{\cdot}] \times [OH']}{[NH_4OH]} = K_B \text{ (ionization constant of base)}$$

whence

$$[OH'] = K_B \times \frac{[NH_4OH]}{[NH_4^{\cdot}]}$$

$$= K_B \times \frac{x}{1-x}$$

For the ionic product of water we have

$$K_W = [H^{\cdot}] \times [OH']$$

$$= K_A \times K_B \times \frac{x^2}{(1+x)^2} \qquad (2)$$

From equations (1) and (2) we get

$$K_H = \frac{x^2}{(1-x)^2} = \frac{K_W}{K_A \times K_B}$$

Since the dilution V cancels out of the hydrolysis equation, *the degree of hydrolysis of a salt of a weak acid and a weak base is independent of the dilution.*

Example 16. *The ionization constant for acetic acid is* $1{\cdot}8 \times 10^{-5}$, *and the ionic product for water is* 10^{-14}. *Calculate the degree of hydrolysis of sodium acetate in N/1000 solution.*

If x is the degree of hydrolysis, we have

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

$$\frac{1-x}{1000} \qquad \frac{x}{1000} \qquad \frac{x}{1000}$$

$$\therefore \frac{x^2}{1-x) \times 1000} = K_H = \frac{K_W}{K_A} = \frac{10^{-14}}{1-8 \times 10^{-5}} = 5{\cdot}56 \times 10^{-10}$$

Since the ionization constant for acetic acid is very much bigger than the ionic product for water, we may put $1-x=1$ (see Note, p. 160).

$$\frac{x^2}{1000} = 5{\cdot}56 \times 10^{-10}$$

$$x^2 = 55{\cdot}6 \times 10^{-8}$$

$$x = {\cdot}000745.$$

Example 17. *At* 25° *the dissociation constant of aniline is* $4{\cdot}8\times10^{-10}$ *and of acetic acid* $1{\cdot}8\times10^{-5}$. *The ionic product for water at this temperature is* $1{\cdot}2\times10^{-14}$. *Calculate (a) the hydrolysis constant of aniline acetate, and (b) the degree of hydrolysis of the salt in a decinormal solution.*

Since both aniline and acetic acid are weak electrolytes, the hydrolysis constant, K_H, of aniline acetate, and its degree of hydrolysis in a solution of *any* concentration is given by the relation

$$K_H = \frac{K_W}{K_A \times K_B} = \frac{x^2}{(1-x)^2}$$

Hence,
$$K_H = \frac{1{\cdot}2\times10^{-14}}{1{\cdot}8\times10^{-5}\times4{\cdot}8\times10^{-10}}$$
$$= \mathbf{1{\cdot}39.}$$

Again, $\frac{x^2}{(1-x)^2} = K_H = 1{\cdot}39$

$$\therefore \frac{x}{1-x} = \sqrt{1{\cdot}39} = 1{\cdot}18$$
$$x = \mathbf{0{\cdot}541.}$$

Example 18. *At* 25° *the partition coefficient of aniline between benzene and water is* 10. *In an experiment* 250 *c. c. of* ·03*N solution of aniline hydrochloride was throughly shaken with* 15 *c. c. of benzene.* 10 *c. c. of the benzene layer were found to contain* ·006 *gram of aniline. Given that the ionic product for water at* 25° *is* $1{\cdot}2\times10^{-14}$, *calculate (i) the hydrolysis constant of aniline hydrochloride, (ii) the degree of hydrolysis in an N/20 solution, and (iii) the the ionization constant of aniline as a base.*

I. CALCULATION OF THE MOLAR CONCENTRATION OF ANILINE HYDROCHLORIDE, FREE ANILINE, AND FREE HCl :—

10 c. c. of the benzene layer contained ·006 gm. of aniline.

Partition coefficient of aniline between benzene and water = 10

∴ Quantity of *free* aniline present in 10 c. c. of the aqueous solution

$$= \cdot 006 \times \frac{1}{10} = \cdot 0006 \text{ gm.}$$

The molecular weight of aniline, $C_6H_5NH_2$, is 93.

$$= \frac{\cdot 0006 \times 100}{93} = \text{mol.}$$

Hence, the concentration of *free* aniline in the aqueous solution

$$= \frac{\cdot 0006 \times 100}{93} = \cdot 00063 \text{ mol. per litre.}$$

Total concentration of aniline (both free and combined) originally present in the solution was ·03 mol. per litre.

Amount of aniline extracted by 15 c. c. of benzene from 250 c. c. of aqueous solution

$$= \cdot 006 \times \frac{15}{10} = \cdot 009 \text{ gm.}$$

Hence the quantity of aniline extracted by benzene

$$= \frac{\cdot 009 \times 1000}{250 \times 93} = \cdot 00039 \text{ mol. per litre.}$$

∴ Total concentration of aniline (both free and combined) in the aqueous layer at equilibrium

$$= \cdot 03 - \cdot 00039 = \cdot 02961 \text{ mol. per litre.}$$

Hence the concentration of *aniline hydrochloride* at equilibrium

$$= \cdot 02961 - \cdot 00063 = \cdot 02898 \text{ mol. per litre.}$$

Now benzene extracts only free aniline, and not aniline hydrochloride or HCl, from the aqueous solution. Hence the *total* concentration of HCl (both free and combined) at equilibrium is the same as that of aniline hydrochloride originally present, *viz.* ·03 mol. per litre. Out of this ·02898 mol. exists as aniline hydrochloride. Hence, the concentration of *free* HCl at equilibrium

$$= \cdot 03 - \cdot 02898 = \cdot 00102 \text{ mol. per litre.}$$

II. CALCULATION OF HYDROLYSIS CONSTANT :—

By definition, the hydrolysis constant K_H

$$= \frac{[\text{free acid}] \times [\text{free base}]}{[\text{unhydrolyzed salt}]}$$

$$= \frac{\cdot00102 \times \cdot00063}{\cdot02898}$$

$$= \mathbf{2 \cdot 12 \times 10^{-5}}$$

III. CALCULATION OF THE DEGREE OF HYDROLYSIS:—

The volume V of the solution which contains 1 mol. of aniline hydrochloride = 20 litres

The degree of hydrolysis x may be calculated from the formula

$$K_H = \frac{x^2}{(1-x)V}$$

which, since the value of K_H is very small, may be used in its simplified form.

$$K_H = \frac{x^2}{V}$$

From this we get

$$x = \sqrt{K_H \times V} = \sqrt{2 \cdot 12 \times 10^{-5} \times 20} = \mathbf{2 \cdot 06 \times 10^{-2}}$$

IV. CALCULATION OF THE IONIZATION CONSTANT K_B

From the relation $K_H = \frac{K_W}{K_B}$ we get

$$K_B = \frac{K_W}{K_H} = \frac{1 \cdot 2 \times 10^{-14}}{2 \cdot 12 \times 10^{-5}} = \mathbf{5 \cdot 65 \times 10^{-10}}$$

54. Solubility Product and Solubility. A saturated solution of a sparingly soluble electrolyte is an extremely dilute solution, and the ionization of the dissolved electrolyte is practically complete. Thus in the case of a saturated solution of silver chloride we have :

$$\mathbf{AgCl} \rightleftharpoons \mathbf{Ag^{\cdot}} + Cl'$$

(solid) (dissolved)

Since the active mass of the solid is constant, it follows from the mass-action law that

$$[Ag^{\cdot}] \times [Cl'] = K \times [AgCl] = L$$

where the square brackets denote the concentration of the enclosed ions or molecules, the former in gram-ions per litre and the latter in mols. per litre. The constant L is termed the **solubility product** for silver chloride.

Since in pure aqueous solution $[Ag^{\cdot}] = [Cl']$, we have

$$[Ag^{\cdot}] = [Cl'] = L = s$$

where s is the **molar solubility**, of silver chloride, *i.e.*, solubility of the salt in mols. per litre. Hence, if the solubility of a sparingly soluble binary electrolyte is known, we can calculate its solubility product from the above relation. Conversely, the solubility of the electrolyte may be calculated from the solubility product.

If we increase the concentration of silver ions, that of the chlorine ions must decrease until the product of the concentrations reaches the solubility product. Similarly, on increasing the concentration of chlorine ions, that of the silver ions will fall until the product of the concentrations is the same as before.

Let us now consider the case of a ternary electrolyte, *e.g.*, that of silver sulphide :

$$Ag_2S \rightleftharpoons 2Ag^{\cdot} + S''$$

By the mass action law we have :

$$[Ag^{\cdot}]^2 \times [S''] = L$$

and since in pure aqueous solution two silver ions are formed for one sulphide ion, the concentration of the latter in gram-ions per litre is one-half that of the former. Hence,

$$[Ag^{\cdot}]^2 \times \tfrac{1}{2}[Ag^{\cdot}] = \tfrac{1}{2}[Ag^{\cdot}]^3 = L$$

or

$$4[S''] \times [S''] = 4[S'']^3 = L$$

The solubility s of silver sulphide in gram-ions per litre is given by the relation

$$s = [S''] = \tfrac{1}{2}[Ag^{\cdot}] = \sqrt[3]{\frac{Ks}{4}}$$

Example 19. *At* 20° *the solubility of silver chloride in water is* 1×10^{-5} *mol. per litre. What weight of silver chloride will be precipitated, if to* 1 *litre of a saturated solution of the salt a sufficient quantity of* $AgNO_3$ *is added to make the solution decinormal with respect to this latter salt ?*

Since in the saturated solution of silver chloride the ionization is practically complete, we have

$$= [Ag^{\cdot}] = [Cl'] = 1 \times 10^{-5}$$

Hence, the solubility product of silver chloride

$$= 1 \times 10^{-5} \times 1 \times 10^{-5} = 1 \times 10^{-10}$$

When a sufficient quantity of $AgNO_3$ is added to make the solution decinormal with respect to this salt the concentration of silver ions $[Ag^{\cdot}]$ is 10^{-1}. Hence we have

$$[Ag^{\cdot}] \times [Cl'] = 10^{-10}$$

$$10^{-1} \times [Cl'] = 10^{-10}$$

$$\therefore \quad [Cl'] = \frac{10^{-10}}{10^{-1}} = 10^{-9}$$

Thus we find that the amount of silver chloride in the solution falls from 10^{-5} to 10^{-9} mols. per litre. Hence the quantity of the salt precipitated on the addition of silver nitrate

$$= 10^{-5} - 10^{-9} = \cdot 000009999 \text{ gram-molecule}$$

$$= \cdot 000009999 \times 143 \cdot 5 \text{ gm.}$$

$$= \mathbf{\cdot 001435 \text{ gm.}}$$

Example 20. *At* 24·5° *the solubility of silver bromate is* ·0081 *mol. per litre. To* 1 *litre of a saturated solution of silver bromate a sufficient quantity of silver nitrate is added to make the solution* ·0085 *normal with respect to silver nitrate. Calculate the strength of the resulting solution with respect to silver bromate, assuming that both the salts are completely ionized in the solution.*

Since in the saturated silver bromate solution the concentrations $[Ag^{\cdot}]$ and $[BrO_3']$ are both ·0081 gram-ion per litre, the solubility product of $AgBrO_3$ is

$$\cdot 0081 \times \cdot 0081 = \cdot 0000656$$

Let the concentration of the mixed solution with respect to silver bromate be x mol. per litre. Then we have

$$[Ag^{\cdot}] = \cdot 0085 + x$$

$$[BrO'_3] = x$$

$$\therefore \quad [Ag^{\cdot}] \times [BrO_3'] = (\cdot 0085 + x)x = \cdot 0000656$$

whence $$x = \cdot \mathbf{0049}.$$

Example 21. *At 20°C the specific conductivity of pure water is* $1{\cdot}5 \times 10^{-6}$ *r.o. and that of a saturated solution of silver chloride* $3{\cdot}0 \times 10^{-6}$ *r.o. The equivalent conductivities of* $AgNO_3$, KCl, *and* KNO_3 *at infinite dilution are* 152, 170, *and* 164 *r.o. respectively. Calculate (i) the solubility of AgBr at* 20° *and (ii) its solubility product.*

(*i*) CALCULATION OF THE SOLUBILITY OF SILVER CHLORIDE AT 20°.

The specific conductivity, κ, due to AgCl alone is equal to total specific conductivity minus the specific conductivity of the water used; *i.e.*

$$\kappa = 3{\cdot}0 \times 10^{-6} - 1{\cdot}5 \times 10^{-6} = 1{\cdot}5 \times 10^{-6} \text{ r.o.}$$

Let s be the solubility of AgCl in gram-equivalents per litre.

Volume, V, of the solution in c.cs. which contains 1 gram-equivalent of $AgCl = \dfrac{1000}{s}$

Equivalent conductivity of the solution

$$= \kappa \times V$$

$$= 1{\cdot}5 \times 10^{-6} \times \frac{1000}{s}$$

Now, since AgCl is almost completely dissociated, the equivalent conductivity calculated as above is equal to equivalent conductivity of AgCl at infinite dilution. This latter is equal to

$$152 + 170 - 164 = 158 \text{ r.o.}$$

Hence, we have

$$1{\cdot}5 \times 10^{-6} \times \frac{1000}{s} = 158$$

whence

$$s = \frac{1{\cdot}5 \times 10^{-6} \times 1000}{158} = 9{\cdot}5 \times 10^{-6} \text{ gram-equivalent per litre.}$$

The equivalent weight of silver chloride is 143·5. Hence, the solubility of silver chloride at 20°

$$9{\cdot}5 \times 10^{-6} \times 143{\cdot}5 = \mathbf{{\cdot}00135 \text{ gm. per litre.}}$$

(*ii*) CALCULATION OF THE SOLUBILITY PRODUCT.

Since silver chloride is completely ionized in the solution, the concentration of both $Ag^{\cdot}$ and Cl' ions is $9{\cdot}5 \times 10^{-6}$ gram ion per litre. Hence the solubility product of the salt

$$= (9{\cdot}5 \times 10^{-6})^2 = \mathbf{9{\cdot}025 \times 10^{-11}}.$$

EXERCISES

1. An electric current is passed between platinum electrodes through solutions of copper sulphate, silver nitrate and dilute sulphuric acid, the solutions being placed in series. Explain what happens in each case. If 0·105 gm. of copper is deposited by the current from the first solution, calculate (*a*) the weight of silver separated from the second solution, (*b*) the volume of hydrogen measured at 15°C., and 740 mm. which is liberated from the third solution. (H = 1 ; Cu = 63·5 ; Ag = 108).

(*Northern Universities Higher School Certificate.*)

2. The same electric current is passed through acidulated water and a solution of the chloride of metal X. The volume of hydrogen liberated (at N.T.P.), was 14·8 litres and the weight of metal deposited 42 gm. The specific heat of the metal is 0·094. Find the formula of the chloride.

(*London Inter. Coll. Schol Board.*)

3. State the Laws of Electrolysis. The same current is passed through acidulated water and a solution of stannous chloride. What volume of detonating gas,

measured dry at 0°C. and under 760 mm. pressure, is evolved from the water when 1 gm. of tin is deposited from the other solution ? (Sn = 119 ; H = 1 ; O = 16.)
(*London Inter. Coll. Schol. Board.*)

4. A current is passed through two electrolytic cells in series containing, respectively, dilute sulphuric acid and a fused aluminium salt. What weight of aluminium will be obtained when 10 litres of detonating gas (at N. T. P.) have been evolved from the dilute sulphuric acid ? (H = 1; O = 16 ; Al = 27.) (*London Inter. B. Com.*)

5. The specific conductivity of a solution of sodium chloride containing 0·585 gm. of the salt per 100 c. c. is found to be ·00865 rec. ohms. The equivalent conductivity of the salt at infinite dilution is 103. Calculate the degree of dissociation of sodium chloride in the given solution.

6. The specific conductivity of a solution of acetic acid containing 7·50 grams of the acid per litre is found to be ·000543 rec. ohms. Calculate the degree of ionization of the acid in the solution, conductivity at infinite dilution for acetic acid being 364 units.

7. The equivalent conductivity of a solution of acetic acid containing 1 gram-molecule of the acid in 128 litres is 16·99. Calculate the freezing point of the solution. *K* for water is 18·6 and $\lambda \infty$ of acetic acid is 364.

8. The equivalent conductivity of a seminormal hydrochloric acid solution is found to be 331 reciprocal ohms. Calculate the degree of ionization and the freezing point of the solution, assuming $\lambda \infty$ for hydrochloric acid to be 378.

9. The equivalent conductivity of a solution of acetic acid at infinite dilution is 388 rec. ohms. The equivalent conductivity of a solution containing 0·3 gm. of acetic acid in 50 c. c. of water is 4·6 rec. ohms. Calculate the freezing point of this solution. (A solution of 34·2 gms. of cane sugar in 100 gms. of water freezes at − 1·85°C.)
(*Selwyn College, Cambridge.*)

10. A current which deposited 0·123 gm. of silver in a silver voltameter was passed through a solution of

silver nitrate containing 1 gm. of the salt per 100 c. c. After electrolysis the anode solution was found to weigh 42·5 gm. and to contain 0·332 gm. of silver. Calculate the ratio of the speeds of the silver and the nitrate ions and their respective transport numbers.

11. A solution of sodium chloride containing ·022 per cent. of chlorine was electrolyzed between a cadmium anode and a platinum cathode, a silver voltameter being placed in series with the electrolytic apparatus. After electrolysis the anode solution was found to weigh 201·0 gm. and to contain ·0483 gm. of chlorine. The weight of silver deposited in the voltameter was ·0398 gm. Calculate the transport numbers of sodium and chlorine ions.

Note. When a cadmium anode is used, the chlorine is not liberated as such, but forms cadmium chloride which remains in solution.

12. During the electrolysis of a solution of silver nitrate it was found that after 0·1259 gm. of silver had been deposited at the cathode, the solution had altered in concentration. On precipitating with sodium chloride the silver contained in 20 c. c. of the cathode solution the following data were obtained: weight of silver chloride (before electrolysis) 1·746 gm., weight of silver chloride (after electrolysis) 1·677 gm. Determine the transport ratio of the silver and the nitrate ions.

(*Trinity Group, Cambridge.*)

13. The equivalent conductivity at infinite dilution for $CuSO_4$ is 120 rec. ohms., and the transport number of the cuprion in the salt is 0·41. Calculate the mobility of the cuprion and the sulphate ion.

14. At 18°C, $\lambda\infty$ for cupric sulphate and silver nitrate is 114 and 116 rec. ohms respectively. If the transport numbers for the cupric and the silver ions in these salts be 0·41 and 0·48 respectively, calculate $\lambda\infty$ for cupric nitrate.

15. Bredig determined the molecular conductivities of ammonia solutions containing one mole of the base in v litres. His results are given below :—

	v in litres	Molecular conductivity.
(*i*)	8	3·20
(*ii*)	16	4·45
(*iii*)	32	6·28
(*iv*)	64	8·90
(*v*)	128	12·63

The conductivity at infinite dilution for ammonia is 237. Show that these results are in accord with Ostwald's Dilution Law.

16. The molecular conductivity of a solution containing one gram-molecule of propionic acid in 8 litres is found to be 3·65. Calculate the ionisation constant and the molecular conductivity of a centinormal solution of the acid, assuming the conductivity at infinite dilution to be 359.

Note. You may use the simplified form of the Dilution Law for this calculation.

17. At 25°C the specific conductivity of a solution containing one-sixteenth of a mol. of ethylamine per litre is $1{\cdot}312 \times 10^{-3}$ mho. The equivalent conductivity at infinite dilution is 232·6 mho. Calculate the dissociation constant of the base.

At what concentration of ethylamine is the hydroxyl ion ·01 normal ? (*Liverpool ; B. Sc.*)

18. The ionization constant of ammonium hydroxide is $1{\cdot}99 \times 10^{-6}$. Calculate (*i*) the degree of ionization of N/10 NH_4OH, and (*ii*) the fall in hydroxyl ion concentration that would occur on the addition of 1 gram of ammonium chloride to 250 c. c. of N/10 NH_4OH, assuming complete dissociation of the salt in solution.

19. To 10 c. c. of N/10 CH_3COOH ($K = 1{\cdot}8 \times 10^{-5}$), ·0106 gm. of anhydrous sodium acetate was added. Cal

culate the hydrogen ion concentration of the resulting solution, assuming complete dissociation of the salt.

20. In an N/100 solution of an acid the degree of ionization is 3·87 per cent. Calculate (*i*) the hydrion concentration of the solution, (*ii*) its hydroxyl ion concentration, and (*iii*) the *p*H value.

21. The *p*H number of a solution is 5·125. Calculate the hydrion concentration in gram equivalents per litre.

22. The dissociation constant for hydrocyanic acid is $1{\cdot}3 \times 10^{-9}$ and the ionic product for water is 10^{-14}. Calculate the percentage hydrolysis of NaCN in N/100 solution.

23. Calculate the degree of hydrolysis of N/200 sodium benzoate solution. The ionization constant for acetic acid is 6×10^{-5} and the ionic product for water is 10^{-14}.

24. The electrolytic dissociation constant of propionic acid is $1{\cdot}3 \times 10^{-5}$ (concentrations being expressed in gram-equivalents per litre; that of water 10^{-14}. Calculate the hydrogen ion concentration in an N/10 solution of sodium propionate. (*Manchester*; *Hons. Finals.*)

25. At 25° the basic constant, K_B, of urea is $1{\cdot}6 \times 10^{-14}$ and the ionic product of water $1{\cdot}2 \times 10^{-14}$. Calculate (*a*) the hydrolysis constant of urea hydrochloride, and (*b*) the percentage hydrolysis in N/10 solution of the salt.

26. At 25° the ionization constant of acetic acid is $1{\cdot}8 \times 10^{-5}$ and of aniline $4{\cdot}8 \times 10^{-10}$. Kw for water at this temperature is $1{\cdot}2 \times 10^{-14}$. Calculate (*a*) the percentage hydrolysis in N/100 solution of aniline acetate, (*b*) the hydrogen ion concentration in the same solution, and (*c*) the hydrolysis constant.

27. At 25° the ionization constant of acetic acid is, $1{\cdot}8 \times 10^{-5}$ and of ammonium hydroxide $2{\cdot}3 \times 10^{-5}$. The ionic product for water at this temperature is $1{\cdot}2 \times 10^{-14}$. Calculate (*a*) the hydrolysis constant of ammonium acetate, (*b*) its degree of hydrolysis in an N/100 solution.

28. At 25° the specific conductivity of pure water is $1{\cdot}52 \times 10^{-6}$ rec. ohms. and that of a saturated solution of silver bromide $1{\cdot}58 \times 10^{-6}$ rec. ohms. The equivalent conductivities of KBr, $AgNO_3$. and KNO_3 at infinite dilution are 137, 121, and 131 rec. ohms. respectively. Calculate (*i*) the solubility of AgBr at 25° and (*ii*) its solubility product.

29. At 25°C the solubility of benzoic acid is 3·4 grams per litre and its ionization constant is $6{\cdot}0 \times 10^{-5}$. Calculate the solubility of the acid in an N/100 solution of sodium benzoate, assuming complete ionization of the salt.

30. At 15°C the solubility of AgCl is ·0015 gm. per litre. Calculate the loss of silver chloride that would occur if a precipitate of the salt be washed with (*i*) 1 litre of water, and (*ii*) 1 litre of N/50 HCl.

31. The solubility of barium sulphate is $2{\cdot}3 \times 10^{-4}$ gm. per 100 c.c. of water. What is the percentage error involved in washing a precipitate of 0·200 gm. $BaSO_4$ with (*a*) 1 litre of water, (*b*) 1 litre of N/100 H_2SO_4.

(Trinity Group, Cambridge.)

32. At 20° the solubility of barium oxalate is ·09 gm. per litre. Calculate the weight of barium oxalate that would be precipitated by adding 2 c.c. of a 2N solution of sodium oxalate to 1 litre of the saturated solution, assuming complete ionization of the salt and neglecting the increase in volume of the solution.

33. 1 litre of a saturated solution of calcium sulphate at 18° contains 0·015 mol of the salt. Calculate how much calcium sulphate should be precipitated by the addition of 0·025 mol of potassium sulphate to 1 litre of this saturated solution, both salts being regarded as practically completely ionized.

(Trinity College, Cambridge.)

34. A saturated aqueous solution of PbI_2 at 25°C contains ·00165 mol of the salt per litre. What will be the solubility of PbI_2 at the same temperature in a 0·1 N solution of NaI?

(Liverpool B. Sc.)

Answers.

1. 0·357 gm.; 39·8 c.c. **2.** XCl_2. **3.** 342·5 c.c.
4. 5·36 gm. **5.** 0·840. **6.** ·00119.
7. −0·0152°C. **8.** 0·876; −1·745°C.
9. −0·1872°C.
10. 0·907; $Ag^{\cdot} = 0{\cdot}476$; $NO_3' = 0{\cdot}524$.
11. $K^{\cdot} = 0{\cdot}494$; $Cl' = 0{\cdot}506$.
12. $Ag^{\cdot}/NO_3' = 0{\cdot}588/0{\cdot}412$.
13. $CO_4'' = 71$.
14. 107. **16.** $K = 1{\cdot}29 \times 10^{-5}$; $\mu = 12{\cdot}9$.
17. $K = 5{\cdot}6 \times 10^{-4}$; 8·5 gm. $C_2H_5NH_2$ per litre.
18. (*i*) ·014; (*ii*) [OH′] falls from 14×10^{-4} to $2{\cdot}7 \times 10^{-5}$ gram-equivalent per litre.
19. $1{\cdot}38 \times 10^{-4}$ gm. per litre.
20. (*i*) $3{\cdot}87 \times 10^{-4}$ gm. equivalent per litre.
(*ii*) $2{\cdot}58 \times 10^{-11}$ gm. equivalent per litre.
(*iii*) 3·42.
21. $7{\cdot}5 \times 10^{-6}$. **22.** 2·74%.
23. $x = 18{\cdot}3 \times 10^{-5}$.
24. $1{\cdot}14 \times 10^{-9}$ gm. per litre.
25. (*a*) 0·75; (*b*) 89°/₀.
26. (*a*) 54°/₀; (*b*) $2{\cdot}12 \times 10^{-5}$ gram-ion per litre; (*c*) 1·4.
27. (*a*) $2{\cdot}9 \times 10^{-5}$ (*b*) ·0054.
28. (*i*) $4{\cdot}7 \times 10^{-7}$ gm. equivalent per litre, or $8{\cdot}84 \times 10^{-5}$ gm. per litre.
(*ii*) $2{\cdot}21 \times 10^{-13}$.
29. 3·27 gm. per litre.
30. (*i*) $1{\cdot}5 \times 10^{-3}$ gm.; (*ii*) $7{\cdot}8 \times 10^{-7}$ gm.
31. (*a*) 1·15 °/₀; (*b*) = ·00227 °/₀.
32. ·0727 gm. **33.** 0·816 gm.
34. $1{\cdot}8 \times 10^{-6}$ mol per litre.

CHAPTER IX

ELECTROMOTIVE FORCE

55. Definition. *The electromotive force between two points is the amount of energy used up in conveying one unit of electricity from one of these points to the other.*

The unit of electromotive force is called a **volt**, which represents the energy in joules (10^7 ergs) used up in conveying one coulomb of electricity, *i. e.*

$$\text{E.M.F. in volts} = \frac{\text{Energy in Joules}}{\text{Electricity in Coulombs}}$$

56. Electrolytic Solution Pressure. When a bar of a metal is placed in contact with a solution of a salt of the metal, say zinc in a solution of zinc sulphate. it is found to possess a **solution pressure**, in virtue of which it tends to lose electrons and form ions. At the same time the ions of the metal present in the solution exert an **osmotic pressure**, and tend to deposit on the metal. As a result of the first change,

$$Zn^0 \longrightarrow Zn^{\cdot\cdot} + 2e,$$

the zinc bar (because of the free electrons left on it) acquires a negative charge, while the solution, containing the zinc ions thrown off by the metal, acquires a positive charge. The tendency of the zinc to go into solution is opposed by the osmotic pressure of the ions. The definite osmotic pressure that just counterbalances this solution tension is known as the **electrolytic solution pressure** or "electrolytic solution tension" of the ions.

On account of the relatively large magnitude of the charge involved, the ions do not move away from the oppositely charged metallic bar, but form an **electrical double layer**, consisting of electrons on the metal and the zinc ions adjacent to the metal. The attraction of the opposite charges prevents the further expulsion of positive ions from the metal, and thus there is rapidly esta-

blished an equilibrium with a definite potential difference, known as **electrode potential**, when only a very few ions of the metal have entered the liquid. Hence, though the solution pressure of the metal may be considerable, the amount of the metal that goes into solution is so minute as not to be detectable by chemical analysis.

57. Calculation of Potential Difference from Osmotic Pressure. Let a metal with a valence n and electrolytic solution pressure P be placed in contact with a solution of its ions at an osmotic pressure p at the temperature T° absolute, and let E be the potential difference set up between the metal and the solution. By connecting this electrode with another, more positive, electrode (which needs no further consideration) we get a cell which may be made to produce n faradays (F) of electricity by the dissolution of 1 gram ion of the metal. This will result in the expenditure of EnF volt-coulombs of electrical energy at the electrode under consideration.

Let us suppose that the solution is now diluted so that the osmotic pressure gets reduced to $p - dp$. The difference of potential between the metal and the solution now changes to $E - dE$. Hence the electrical energy that must be expended to cause the dissolution of 1 gram ion of the metal will now be $(E - dE)nF$ volt-coulombs.

In the first case, 1 gram-ion of the metal goes into solution at osmotic pressure p and in the second case at an osmotic pressure $p - dp$. The difference in electrical work must (according to the first law of Thermodynamics) be equal to the osmotic work of transfer of 1 gram-ion from an osmotic pressure of p to one of $p - dp$. If V is the volume of the solution containing 1 gram-ion of metal, this osmotic work will be equal to $V\,dp$. Hence, we have :

$$EnF - (E - dE)nF = V\,dp$$

or,
$$nF.\,dE = V\,dp \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Now, since the solution may be assumed to obey the gas law, $PV = RT$, or $V = RT/P$.

Substituting this value of V in equation (1) we get

$$nF.\ dE = RT.\frac{dp}{p} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

On integrating equation (2) we get

$$nFE = RT\ log\ p + K \ldots\ldots\ldots\ldots (3)$$

where K is the integration constant. When the osmotic pressure p of the solution equals the electrolytic solution pressure P of the metal, there exists no difference of potential between the metal and the solution ; *i. e.* $E=0$. Equation (3) in this case becomes

$$0 = RT\ log\ P + K$$

whence $$K = -RT\ log_e P$$

Substituting this value of K in equation (3) we get

$$nFE = RT\ log_e p - RT\ log_e P$$

$$= RT\ log\ \frac{p}{P}$$

$$\therefore \mathbf{E = \frac{RT}{nF}\ log\ \frac{p}{P}} \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Equation (4) is known as **Nernst's equation** for the potential of an electrode. It may be simplified for practical purposes as given below.

F. as we already know, is one faraday or 96540 coulombs, the charge carried by 1 gram-equivalent of any ion. When the unit of energy is volt-coulomb or joule, the numerical value of R is $2 \times 4{\cdot}16$ or $8{\cdot}32$*. Further, since the factor for the reduction of log to $\log_{10}$ is $2{\cdot}303$, the equation (4) becomes

$$E = \frac{8{\cdot}32 \times T \times 2{\cdot}303}{n \times 96540}\ log\ \frac{p}{P}$$

$$\mathbf{E = \frac{1.985 \times 10^{-4} \times T}{n}\ log\ \frac{p}{P}} \ldots\ldots\ldots\ldots (5)$$

---

*R is approximately equal to 2 calories (p. 61) and 1 calorie is equal to 4·16 Joules.

For 18°C (T = 291° absolute) the expression becomes

$$E = \frac{1{\cdot}985 \times 10^{-4} \times 291}{n} \log \frac{p}{P}$$

$$\mathbf{E = \frac{{\cdot}058}{n} \log \frac{p}{P} \text{ volt}} \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

The constant in equation (6) varies with the temperature ; e. g. its value at 25°C (or 298° absolute) is about ·059.

The *sign* of the electrode potential, E, depends on the relative values of P and p. When the former is greater (as in the case of zinc, etc.) $\log \frac{p}{P}$ and, therefore, E will be negative. When P is smaller than p, E will be positive. If P happens to be equal to p, $\log \frac{p}{P}$ will be zero, and hence no potential difference will exist

58. E. M. F. of a Concentration Cell.

Let us consider the following cell :

I			II
Ag	$AgNO_3$ solution with c_1 as gram-ion concentration per litre and p_1 osmotic pressure.	$AgNO_3$ solution with c_2 as gram-ion concentration per litre and p_2 osmotic pressure (more concentrated).	Ag

There will exist a potential difference

(*i*) between metal and solution with p_1 osmotic pressure,

(*ii*) between the two solutions (i. e. the **diffusion potential**),

(*iii*) between solution with p_2 osmotic pressure and metal.

The potential difference (*ii*) between the two solutions is small and can be eliminated by using a neutral solution, e. g. a saturated ammonium nitrate solution, as a bridge between the two. Then, since n = 1, we have :

$$\text{P. D. } (i) = \cdot 058 \log \frac{p_1}{P}$$

$$\text{P. D. } (iii) = \cdot 058 \log \frac{p_2}{P}$$

Now, since p_2 is greater than p_1, the electrode II will be at a higher potential, the current *through* the cell flowing from I to II, and in the outer circuit from II to I. Electrode I thus acts as the negative electrode.

The resulting electromotive force of the cell will be $(iii) - i)$; i. e.

$$\text{E. M. F.} = \cdot 058 \log \frac{p_2}{P} - \cdot 058 \log \frac{p_1}{P} \text{ volt}$$

$$= \cdot 058 \log \frac{p_2}{p_1} \text{ volt}$$

$$= \cdot 058 \log \frac{c_2}{c_1} \text{ volt}$$

If, for instance, $c_2 = 10c_1$, E. M. F. of the cell will be equal to ·058 volt.

In general, if the valency of the ion present in solution is n, the electromotive force of the cell will be

$$\textbf{E. M. F.} = \frac{\cdot 058}{n} \log \frac{c_2}{c_1} \text{ volt} \ldots\ldots\ldots\ldots (7)$$

Example 1. *Find the potential difference between the metal electrodes in cell*

$$Ag \left| \frac{N}{200} AgNO_3 \right| \begin{matrix} Saturated \\ NH_4NO_3 \ solution \end{matrix} \left| \frac{N}{20} AgNO_3 \right| Ag$$

at 18°, if N/20 and N/200 $AgNO_3$ are 86 per cent and 95 per cent dissociated. The ammonium nitrate merely eliminates diffusion potential between the two solutions.

(*Punjab B. Sc. 1932.*)

The concentration, c_1, in gram-ions of silver, in N/200 $AgNO_3$

$$= \frac{1}{200} \times \frac{95}{100} = \cdot 00475$$

Similarly, c_2, the gram-ion concentration of N/20 $AgNO_3$

$$= \frac{1}{20} \times \frac{86}{100}$$
$$= \cdot 043$$

$\therefore$ Potential difference between the two electrodes

$$= \cdot 058 \log \frac{c_2}{c_1} \text{ volt}$$
$$= \cdot 058 \log \frac{\cdot 043}{\cdot 00475} \text{ volt}$$
$$= \mathbf{\cdot 0555 \text{ volt.}}$$

Note.—In the above case the current will flow *through* the cell from left to right i. e. from the weaker to the more concentrated solution, the electrode in contact with the latter being at a higher potential. In the outer circuit the current will, of course, flow from right to left.

Example 2. *The E. M. F. of the cell.*

$$Cu \left| \begin{matrix} N/5\ Cu\ SO_4 \\ (34\ \%\ dissociated) \end{matrix} \right| ?\ Cu\ SO_4 \left| Cu \right.$$

is ·08 *volt. Calculate the concentration of the unknown solution, assuming it to be completely dissociated.*

The gram-ion concentration of N/5 $CuSO_4$

$$= \frac{1}{5} \times \frac{34}{100} = \cdot 068$$

Let the gram-ion concentration of the unknown $CuSO_4$ solution be c.

Since the unknown solution is assumed to be completely dissociated, it must be very dilute, and the value of c much lower than ·068.

The E. M. F. of the cell is ·08 volt.

Substituting the above values in the equation,

$$\text{E. M. F.} = \frac{\cdot 058}{n} \log \frac{c_2}{c_1} \text{ volt,}$$

where c_2 is greater than c_1, we get

$$\cdot 08 = \frac{\cdot 058}{2} \log \frac{\cdot 068}{c}$$

or,
$$\log c = -\frac{\cdot 08}{\cdot 029} + \log \cdot 068$$
$$= -2\cdot 76 + 2\cdot 8325$$
$$= \bar{4}\cdot 0725$$
$$\therefore c = \cdot 00012$$

Hence, the concentration of the unknown $CuSO_4$ solution is **·00012N.**

Example 3. *The E. M. F. of the cell*

$$Ag \mid N/10\ AgNO_3 \mid N/500\ AgNO_3 \mid Ag$$

is ·094 volt. Assuming N/10 $AgNO_3$ to be 81 per cent dissociated, calculate the degree of dissociation of N/500 $AgNO_3$.

Let the degree of dissociation of N/500 $AgNO_3$ be x per cent.

The gram-ion concentration of $Ag^{\cdot}$ in N/10 $AgNO_3$

$$= \frac{1}{10} \times \frac{81}{100} = \cdot 081.$$

The gram-ion concentration of $Ag^{\cdot}$ in N/500 $AgNO_3$

$$= \frac{1}{500} \times \frac{x}{100}$$

The E. M. F. of the cell is ·094 volt.

Substituting the above values in the equation,

$$\text{E. M. F.} = \frac{\cdot 058}{n} \log \frac{c_2}{c_1} \text{ volt},$$

where c_2 is greater than c_1, we get

$$\cdot 094 = \frac{\cdot 058}{1} \log \frac{\cdot 081}{\frac{x}{50000}}$$

or,
$$\frac{\cdot 094}{\cdot 058} = \log \frac{4050}{x}$$

$$= \log 4050 - \log x$$

$$\therefore \log x = \log 4050 - \frac{\cdot 094}{\cdot 058}$$

$$= 3\cdot 6075 - 1\cdot 6207$$

$$= 1\cdot 9868$$

$$\therefore x = 97$$

Hence, the degree of dissociation of N/500 $AgNO_3$ solution is **97**°/₀.

Example 4. *The E. M. F. of the following cell at 18° is 0·488 volt.*

	N/100 $AgNO_3$	*Saturated*	*Saturated*	
Ag		*NH_4NO_3*	*AgBr solution in N/100 K Br*	*Ag*

Given that N/100 $AgNO_3$ and N/100 KBr are respectively 93 and 94 per cent dissociated, calculate the solubility product of AgBr and its solubility in grams per litre.

Let the gram-ion concentration of silver ion in the saturated AgBr solution in N/100 KBr be *c*.

The gram ion concentration of silver ion in N/100 $AgNO_3$.

$$= \frac{1}{100} \times \frac{93}{100} = \cdot 0093$$

The E. M. F. of the cell is 0·488.

Substituting these values in the equation,

$$\text{E. M. F.} = \frac{\cdot 058}{n} \log \frac{c_2}{c_1} \text{ volt,}$$

where c_2 is greater than c_1, we get

$$0\cdot 488 = \frac{\cdot 058}{1} \log \frac{\cdot 0093}{c}$$

Whence, $c = 3\cdot 6 \times 10^{-11}$

Now, the gram-ion concentration of bromion in N/100 KBr

$$= \frac{1}{100} \times \frac{94}{100} = \cdot 0094$$

Hence, the solubility product,

$$[Ag^{\cdot}] \times [Br'] = 3{\cdot}6 \times 10^{-11} \times {\cdot}0094$$
$$= \mathbf{3{\cdot}384 \times 10^{-13}}$$

∴ The concentration of silver ion (or bromion) in saturated AgBr solution

$$= \sqrt{3{\cdot}384 \times 10^{-13}} \text{ gm-ion}$$
$$= 5{\cdot}8 \times 10^{-7} \text{ gm-ion}$$

∴ Solubility of AgBr

$= 5{\cdot}8 \times 10^{-7}$ gram molecule per litre.

$= 5{\cdot}8 \times 10^{-7} \times 188$ gm. per litre.

$= \mathbf{1{\cdot}09 \times 10^{-4}}$ " "

59. Standard Electrodes or Standard Half Elements. The E. M. F. of a cell may be regarded as being made up of two parts, called *half elements*, each consisting of an electrode immersed in a suitable solution. For the purposes of comparison it is sometimes necessary to make one of the parts possess a constant value. Such a half element is called a "standard half element" or a "standard electrode". Two of the standard electrodes that are frequently used in the E. M. F. measurements are the hydrogen electrode and the calomel electrode.

60. Hydrogen Electrode. This consists of a strip or wire of platinum covered with a coating of spongy platinum and partially immersed in a solution of HCl. Through this solution and over the electrode is passed a stream of purified hydrogen at atmospheric pressure. The spongy platinum absorbs hydrogen and becomes a "hydrogen electrode". Denoting this by H_2, the E. M. F. of the cell

$$H_2 \mid \text{HCl solution (conc.} = c_1) \mid \text{HCl solution (conc.} = c_2) \mid H_2$$

$\longleftarrow$

may readily be calculated by the formula

$$E = {\cdot}058 \log_{10} \frac{c_2}{c_1} = {\cdot}058 \, (\log_{10} c_2 - \log_{10} c_1)$$

Now $pH_1 = -\log_{10} c_1$, and, $pH_2 = -\log_{10} c_2$ (p. 156)

where pH_1 and pH_2 are the pH values of the two solutions. Hence, we have :

$$E = \cdot 058(p_{H_1} - p_{H_2}) \ldots\ldots\ldots\ldots\ldots (8)$$

A hydrogen electrode immersed in a *normal solution of hydrion* (a little over normal HCl solution) is called a **normal hydrogen electrode**

When used as a reference standard, the potential of a normal hydrogen electrode is taken as zero. The electromotive force E of the following cell

H_2	HCl that is normal with respect to hydrion i. e. $p_{H_1} = 0$	Unknown acid solution ; p_{H_2}	H_2

is given by the relation :

$$E = \cdot 058(p_{H_2} - p_{H_1}) = \cdot 058 p_{H_2}$$

Example 5. *Calculate the E. M. F. of the following cell :--*

H_2	*HCl solution* $p_{H_1} = 3$	*HCl solution* $p_{H_2} = 1 \cdot 5$	H_2

We have the formula

$$E = \cdot 058(p_{H_1} - p_{H_2})$$

Hence the E. M. F. of the above cell

$$= \cdot 058(3 - 1 \cdot 5) \text{ volt}$$
$$= \cdot 87 \text{ volt.}$$

Example 6. *The E. M. F. of the cell*

H_2	*HCl solution* $p_{H_1} = 3 \cdot 2$	*HCl solutirn* p_H *unknown*	H_2

is found to be 0·1 volt. Calculate the p_H *value of the unknown solution.*

We have the formula

$$E = \cdot 058(p_{H_1} - p_H)$$
$$\therefore 0 \cdot 1 = \cdot 058(3 \cdot 2 - p_H)$$

or
$$p_H = 3 \cdot 2 - \frac{0 \cdot 1}{\cdot 058}$$

$= 3\cdot2 - 1\cdot724$
$= 1\cdot476$

61. Normal Calomel Electrode. This is largely used as a standard of potential difference with which other electrodes may be combined for measurement. It consists of a layer of mercury (into which dips a platinum wire for effecting a metallic contact) covered by a layer of calomel over which is placed a normal solution of potassium chloride. When combined with a hydrogen electrode (e. g. in the determination of hydrogen ion concentration) the calomel electrode forms the positive half of the cell, i. e. the current passes through the cell *from the hydrogen to the calomel electrode.*

The potential of the normal calomel electrode at 18°C is 0·282 volt. Other calomel electrodes are also used. The potentials of various calomel electrodes on, what is known as, the **normal hydrogen scale** are as follows :—

Hg.HgCl. Saturated KCl.....0·251 volt
Hg.HgCl. N KCl.....0·2822 „
Hg.HgCl. N/10 KCl.....0·3351 „

Example 7. *Calculate the E. M. F. of the following cell at 18°C*

$$Hg.\ HgCl.\ N\ KCl \ \Big|\ \begin{matrix} N/1000\ HCl \\ (0\cdot985\ dissociated) \\ p_H \end{matrix} \ \Big|\ H_2$$

The E. M. F. of the cell is equal to the sum of the potentials of the two half elements, E_1 of the hydrogen electrode and E_2 of the normal calomel electrode.

The value of E_2 (see above) is 0·2822 volt.
E_1 (see p. 185) is equal to ·058 p_H.

The hydrion concentration of the acid solution
$= ·001 \times 0\cdot985 = ·000985.$

$\therefore$ p_H of the solution $= -\log_{10} ·000985$
$= -(\bar{4}\cdot993)$
$= -(-3\cdot007)$
$= 3\cdot007$

$$\therefore E_1 = 0.058 \times 3.007$$
$$= 0.1744 \text{ volt}$$
$$\text{E. M. F.} = E_1 + E_2 = 0.2822 + 0.1744 \text{ volt}$$
$$= \mathbf{0.4566 \text{ volt.}}$$

Exercises

1. Find the E. M. F. of the cell

$$\text{Ag} \mid \text{N/100 } AgNO_3 \mid \begin{matrix}\text{Saturated} \\ NH_4NO_3\end{matrix} \mid \text{N/1000 Ag } NO_3 \mid \text{ Ag}$$

at 25°C, if N/100 $AgNO_3$ and N/1000 $AgNO_3$ are respectively 96 per cent and 100 per cent dissociated.

2. The E. M. F. of the cell

$$Ag \mid N/5\ AgNO_3 \mid ?AgNO_3 \mid Ag$$

at 18° is .07 volt. Calculate the concentration of the unknown solution, assuming it to be 93 per cent dissociated. N/5 Ag NO_3 is 75 per cent dissociated.

3. Calculate the E. M. F. of the following cell at 18°C,

$$\text{Cu} \mid \text{N/10 } CuSO_4 \mid \begin{matrix}\text{Saturated} \\ NH_4NO_3\end{matrix} \mid \text{N/500 } CuSO_4 \mid \text{Cu}$$

given that N/10 $CuSO_4$ and N/500 $CuSO_4$ are respectively 39 and 81 per cent dissociated. The ammonium nitrate serves simply to eliminate a diffusion potential between the two solutions.

4. The E. M. F. of the cell

$$Zn \mid N/2\ ZnSO_4 \mid N/20\ ZnSO_4 \mid Zn$$

is .018 volt. Neglecting the diffusion potential at the junction of the electrolytes, and assuming the concentrated solution to be 14 per cent dissociated, calculate the degree of dissociation of the dilute solution.

5. The E. M. F. of the following cell at 18° is 0.1 volt

$$\text{Ag} \mid \begin{matrix}\text{Saturated} \\ AgCl\end{matrix} \mid \text{N/2000 } AgNO_3 \mid \text{ Ag}$$

$$\longrightarrow$$

Assuming the solutions to be cempletely dissociated, calculate the solubility of silver chloride at 18°

6. The E. M. F. of the cell

Ag	N/10 Ag NO_3	Saturated Ag Br solution in Normal KBr		Ag

←

at 18°C is 0·64 volt. Find the solubility product and solubility of AgBr at 18°C. N/10 $AgNO_3$ and N KBr are respectively 81·3 and 75·5 per cent dissociated at 18°C.

7. Calculate the E. M. F. of the following cell a 18°C

Ag | N/10 $AgNO_3$ | N/500 $AgNO_3$ | Ag

assuming N/10 $AgNO_3$ and N/500 $AgNO_3$ to be 81 and 97 per cent dissociated.

8. The E. M. F. of the following cell at 18° is 0·51 volt.

Ag	N/10 $AgNO_3$	Normal solution of KCl saturated with AgCl		Ag

Given that N/10 Ag NO_3 and N KI are respectively 81 and 76 per cent dissociated, calculate the solubility product and the solubility of AgCl at 18°C.

9. Find the E. M. F. of the cell

H_2	HCl solution $p_H = 1·293$	HCl solution $p_H = 2·745$	H_2

10. Calculate the E. M. F. of the following cell :—

Hg. HgCl saturated KCl	N/250 HCl $x = 0·97$	H_2

11. Given that the E. M. F. of the following cell at 18°C

Hg. HgCl saturated KCl	N/10 HCl	H_2

is 0·3113 volt, calculate the p_H value and the degree of dissociation of N/10 HCl at the above temperature.

Answers.

1. ·058 volt.
2. N/100.
3. ·04 volt.
4. 35 per cent.
5. $1{\cdot}363 \times 10^{-3}$ gm. per litre.
6. $5{\cdot}67 \times 10^{-13}$; $1{\cdot}416 \times 10^{-4}$ gm. per litre.
7. ·094 volt.
8. $9{\cdot}88 \times 10^{-11}$; $1{\cdot}43 \times 10^{-3}$ gm. per litre
9. ·0842 volt.
10. 0·391 volt
11. $p\mathrm{H} = 1{\cdot}04$; degree of dissociation $= 0{\cdot}99$.

APPENDIX I

IMPORTANT RELATIONS

(1) Mol. Wt. $= 2 \times$ V.D. [p. 33

(2) $\frac{d_1}{d_2} = \frac{t_1^2}{t_2^2}$ [p. 35

(3) $x = \frac{D-d}{d(n-1)}$ [p. 40

(4) $PV = \frac{1}{3}\, nmc^2$ [p. 42

(5) Average Velocity = R.M.S.V. $\times$ 0·9213 [p. 43

(6) γ for a monoatomic gas = 1·67
,, ,, diatomic ,, = 1·41
,, ,, triatomic ,, = 1·33 [p 44

(7) $\gamma = \frac{V^2 D}{P}$ [p. 44

(8) $\gamma = \frac{\log P_1 - \log P}{\log P_1 - \log P_2}$ [p. 45

(9) $PV = RT$ [p. 49

(10) $x = \frac{P-p}{p(n-1)}$ [p. 52

(11) $\frac{p_1 - p_2}{p_1} = \frac{n}{N}$ [p. 54

(12) $\frac{p_1 - p_2}{p_1} = \frac{wM}{mW}$ [p. 54

(13) $\frac{w_1}{w_2} = \frac{p_1 \times 18}{p_2 \times M}$ [p. 58

(14) $\frac{M}{s} = \frac{K}{\Delta}$ [p. 61

(15) $K = \frac{RT^2}{100L}$ [p. 61

(16) Monomolecular reactions :—

$$\frac{1}{t}\log_{10}\frac{a}{a-x}=K$$ [p. 93

(17) Bimolecular reactions :—

$$\frac{1}{t}\times\frac{x}{a(a-x)}=K$$ [p. 98

(18) Trimolecular reactions :—

$$K=\frac{1}{t}\times\frac{x(2a-x)}{2a^2(a-x)^2}$$ [p. 102

(19) $\frac{C_1}{C_2}=K$ [p. 107

(20) $\frac{C_1}{\sqrt[n]{C_2}}=\text{constant}$ [p. 112

(21) 1 Gram-equivalent of a cation or anion is set free by 96540 coulombs (or a faraday). (p. 142

(22) $\alpha=\frac{\lambda v}{\lambda\infty}$ [p. 144

(23) $\frac{\text{Speed of cation}}{\text{Speed of anion}}=\frac{\text{Fall round anode}}{\text{Fall round cathode}}$ [p. 146

(24) $\lambda\infty=u+v$ [p. 150

(25) $\frac{x^2}{V}=K$ [p. 152

(26) $pH=\log_{10}\frac{1}{C}$ [p. 156

(27) Hydrolysis of Salts :—

(*i*) Weak Acid with Strong Base :—

$$K_H=\frac{K_W}{K_A}=\frac{x^2}{(1-x)V}$$ [p. 160

(*ii*) Weak Base with Strong Acid :—

$$K_H=\frac{K_W}{K_B}=\frac{x^2}{(1-x)V}$$ [p. 161

(*iii*) Weak Acid with Weak Base :—

$$K_H=\frac{x^2}{(1-x)^2}=\frac{K_W}{K_A\times K_B}$$ [p. 162

(28) $E = \frac{RT}{nF} \log_e \frac{p}{P}$ [p. 178

(29) $E = \frac{1{\cdot}985 \times 10^{-4} \times T}{n} \log \frac{p}{P}$ [p. 178

When $T = 291^\circ$ absolute (*i.e.*, 18°C) the above relation becomes

$$E = \frac{{\cdot}058}{n} \log \frac{p}{P} \text{ volt}$$

(30) $E.M.F. = \frac{{\cdot}058}{n} \log \frac{c_2}{c_1}$ volt [p. 183

(31) $E = {\cdot}058\ (pH_1 - pH_2)$ [p. 185

APPENDIX II

ATOMIC WEIGHTS

While solving problems, use the *approximate* atomic weights given below :—

Element.	Symbol.	Atomic Weight.	Element.	Symbol.	Atomic Weight.
Aluminium	Al	27	Lead	Pb	207
Antimony	Sb	120	Magnesium	Mg	24
Arsenic	As	75	Manganese	Mn	55
Barium	Ba	137	Mercury	Hg	200
Bismuth	Bi	208	Nickel	Ni	59
Boron	B	11	Nitrogen	N	14
Bromine	Br	80	Oxygen	O	16
Calcium	Ca	40	Phosphorus	P	31
Carbon	C	12	Potassium	K	39
Chlorine	Cl	35·5	Silicon	Si	28
Chromium	Cr	52	Silver	Ag	108
Cobalt	Co	59	Sodium	Na	23
Copper	Cu	63·6	Strontium	Sr	88
Hydrogen	H	1	Sulphur	S	32
Iodine	I	127	Tin	Sn	119
Iron	Fe	56	Zinc	Zn	65

APPENDIX III

TENSION OF WATER VAPOUR IN MILLIMETRES OF MERCURY

Temp °C	Vapour pressure.	Temp. °C	Vapour pressure.	Temp. °C	Vapour pressure.
5	6·5	17	14·4	29	29·8
6	7·0	18	15·4	30	31·5
7	7·5	19	16·3	31	33·4
8	8·0	20	17·4	32	35·4
9	8·6	21	18·5	33	37·4
10	9·2	22	19·7	34	39·5
11	9·8	23	20·9	35	41·8
12	10·5	24	22·2	36	44·2
13	11·2	25	23·5	37	46·7
14	11·9	26	25·0	38	49·3
15	12·7	27	26·5	39	52·0
16	13·5	28	28·1	40	54·9

APPENDIX IV

USEFUL MEMORANDA

One litre = 61 cubic inches = 0·22 gallon = 1·8 pint
= 35·2 fluid oz.

1 Fluid oz. = 28·4 c.c.

1 gram = 15·4 grains.

1 lb. = 453·6 grams. 1 oz. = 28·35 gm.

1 Kilogramme = 2·2 lbs.

APPENDIX V. LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4 9 13 4 8 12	17 21 26 16 20 24	30 34 38 28 32 36
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4 8 12 4 7 11	15 19 23 15 19 22	27 31 35 26 30 33
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3 7 11 3 7 10	14 18 21 14 17 20	25 28 32 24 27 31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3 7 10 3 7 10	13 16 20 13 16 19	23 26 30 22 25 29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3 6 9 3 6 9	12 15 19 12 15 17	22 25 28 20 23 26
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3 6 9 3 6 8	11 14 17 11 14 17	20 23 26 19 22 25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3 5 8 3 5 8	11 14 16 10 13 16	19 22 24 18 21 23
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3 5 8 2 5 7	10 13 15 10 12 15	18 20 23 17 20 22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 5 7 2 5 7	9 12 14 9 11 14	16 19 21 16 18 21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2 4 7 2 4 6	9 11 13 8 11 13	16 18 20 15 17 19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2 4 6	8 11 13	15 17 19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2 4 6	8 10 12	14 16 18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2 4 6	8 10 12	14 15 17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2 4 6	7 9 11	13 15 17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2 4 5	7 9 11	12 14 16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2 3 5	7 9 10	12 14 15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2 3 5	7 8 10	11 13 15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2 3 5	6 8 9	11 13 14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2 3 5	6 8 9	11 12 14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1 3 4	6 7 9	10 12 13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1 3 4	6 7 9	10 11 13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1 3 4	6 7 8	10 11 12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1 3 4	5 7 8	9 11 12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1 3 4	5 6 8	9 10 12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1 3 4	5 6 8	9 10 11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1 2 4	5 6 7	9 10 11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1 2 4	5 6 7	8 10 11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1 2 3	5 6 7	8 9 10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1 2 3	5 6 7	8 9 10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1 2 3	4 5 7	8 9 10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1 2 3	4 5 6	8 9 10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1 2 3	4 5 6	7 8 9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1 2 3	4 5 6	7 8 9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1 2 3	4 5 6	7 8 9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1 2 3	4 5 6	7 8 9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1 2 3	4 5 6	7 8 9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1 2 3	4 5 6	7 7 8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1 2 3	4 5 5	6 7 8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1 2 3	4 4 5	6 7 8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1 2 3	4 4 5	6 7 8

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	5	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	3	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	6
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	5	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

APPENDIX VI. ANTILOGARITHMS

·0	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0 0 1	1 1 1	2 2 2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0 0 1	1 1 1	2 2 2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0 0 1	1 1 1	2 2 2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0 0 1	1 1 1	2 2 2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0 1 1	1 1 2	2 2 2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0 1 1	1 1 2	2 2 2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0 1 1	1 1 2	2 2 2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0 1 1	1 1 2	2 2 2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0 1 1	1 1 2	2 2 3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0 1 1	1 1 2	2 2 3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0 1 1	1 1 2	2 2 3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0 1 1	1 2 2	2 2 3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0 1 1	1 2 2	2 2 3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0 1 1	1 2 2	2 3 3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0 1 1	1 2 2	2 3 3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0 1 1	1 2 2	2 3 3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0 1 1	1 2 2	2 3 3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0 1 1	1 2 2	2 3 3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0 1 1	1 2 2	2 3 3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0 1 1	1 2 2	3 3 3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0 1 1	1 2 2	3 3 3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0 1 1	2 2 2	3 3 3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0 1 1	2 2 2	3 3 3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0 1 1	2 2 2	3 3 4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0 1 1	2 2 2	3 3 4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0 1 1	2 2 2	3 3 4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0 1 1	2 2 3	3 3 4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0 1 1	2 2 3	3 3 4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0 1 1	2 2 3	3 4 4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0 1 1	2 2 3	3 4 4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0 1 1	2 2 3	3 4 4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0 1 1	2 2 3	3 4 4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0 1 1	2 2 3	3 4 4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0 1 1	2 2 3	3 4 4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1 1 2	2 3 3	4 4 5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1 1 2	2 3 3	4 4 5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1 1 2	2 3 3	4 4 5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1 1 2	2 3 3	4 4 5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1 1 2	2 3 3	4 4 5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1 1 2	2 3 3	4 5 5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1 1 2	2 3 4	4 5 5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1 1 2	2 3 4	4 5 5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1 1 2	2 3 4	4 5 6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1 1 2	3 3 4	4 5 6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1 1 2	3 3 4	4 5 6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1 1 2	3 3 4	5 5 6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1 1 2	3 3 4	5 5 6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1 1 2	3 3 4	5 5 6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1 1 2	3 4 4	5 6 6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1 1 2	3 4 4	5 6 6

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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